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An IR study of $(CO_2)_n^+$ (n=3–8) cluster ions in the 1000–3800 cm^{-1} region

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Infrared photodissociation (IRPD) spectra of carbon dioxide cluster ions, $(CO_2)_n^+$ with $n=3-8$, are measured in the 1000–3800 cm^{-1} region. IR bands assignable to solvent CO_2 molecules are observed at positions close to the vibrational frequencies of neutral CO_2 [1290 and 1400 cm^{-1} (ν_1 and $2\nu_2$), 2350 cm^{-1} (ν_3), and 3610 and 3713 cm^{-1} ($\nu_1+\nu_3$ and $2\nu_2+\nu_3$)]. The ion core in $(CO_2)_n^+$ shows several IR bands in the 1200–1350, 2100–2200, and 3250–3500 cm^{-1} regions. On the basis of previous IR studies in solid Ne and quantum chemical calculations, these bands are ascribed to the $C_2O_4^+$ ion, which has a semicovalent bond between the CO_2 components. The number of the bands and the bandwidth of the IRPD spectra drastically change with an increase in the cluster size up to $n=6$, which is ascribed to the symmetry change of $(CO_2)_n^+$ by the solvation of CO_2 molecules and a full occupation of the first solvation shell at $n=6$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2953710]

I. INTRODUCTION

Carbon dioxide cluster ion $(CO_2)_n^+$ is one of the cluster systems that has been extensively studied in the past few decades. Investigation of $(CO_2)_n^+$ includes mass spectroscopy with photoionization and electron-impact ionization,[1–13] photodissociation (PD) spectroscopy,[14–19] infrared (IR) and visible absorption spectroscopy in the gas phase, matrices, and supercritical media,[20–24] and quantum chemical calculations.[25–27] Measurement of thermochemical values for the association reaction, $(CO_2)_{n-1}^+ + CO_2 \rightarrow (CO_2)_n^+$, by high-pressure mass spectrometry gave the binding energy of these clusters.[1,5,10,11] Hiraoka *et al.*[10] estimated the enthalpy change for the association reaction to be 15.6, 5.6, 5.1, 4.8, and 4.0 kcal/mol for $n=2-6$, respectively. The binding energy of $(CO_2)_2^+$ is higher than that of $(CO_2)_n^+$ with $n>2$, suggesting the dimer ion core structure $(CO_2)_2^+ \cdots (CO_2)_{n-2}$. The ionization energy of neutral $(CO_2)_n$ clusters measured by photoionization and electron-impact ionization also provided the binding energies of $(CO_2)_n^+$,[2–4,9,13] which were almost the same as those estimated in the thermochemical measurements. The dimer ion core structure of $(CO_2)_n^+$ was confirmed with PD spectroscopy in the visible region.[14–18] Absorption of $(CO_2)_2^+$ in the visible region is attributed to a transition between two charge resonance (CR) states. Wave functions of the CR states are given by $\Psi_{CR} = \psi(M_a^+) \cdot \psi(M_b) \pm \psi(M_a) \cdot \psi(M_b^+)$, where $\psi(M^+)$ and $\psi(M)$ stand for wave functions of CO_2^+ ($X\ ^2\Pi_g$) and CO_2 ($X\ ^1\Sigma_g^+$), respectively. The existence of the CR transition for $(CO_2)_2^+$ suggests that the positive charge is delocalized over the two CO_2 molecules; the charge-delocalized dimer ion can be expressed as $C_2O_4^+$. The CR transition was observed for the $(CO_2)_n^+$ clusters with $n=2-26$.[16,17] However, due to the structureless feature of the CR transition, it is quite difficult to extract the information on the geometric structure of the dimer ion core itself. IR spectroscopy is thought to give definitive evidence for the structure of ions and molecules. CO_2 has three vibrational modes: ν_1 and ν_3 are the symmetric and antisymmetric CO stretching vibrations and ν_2 is the OCO bending vibration. In the gas phase, the IR band assignable to the ν_3 vibration of the CO_2^+ monomer ion was observed at ~1423 cm^{-1}.[20] This band was also found at almost the same position in solid Ne.[21–23] In addition to the CO_2^+ band, the IR band characteristic of $C_2O_4^+$ appears at ~2131 cm^{-1} in solid Ne.[22,23] On the basis of the IR band position, the $C_2O_4^+$ ion was predicted to have a C_{2h} structure.[22] Quantum chemical calculations of $(CO_2)_2^+$ demonstrated that the C_{2h} structure is more stable than a T-shaped (C_{2v}) isomer.[25,26] Here it is to be noted that density functional theory (DFT) calculations of $(CO_2)_n^+$ with $n=2-4$ predict only isomers in which the positive charge is delocalized over all the constituent molecules even for $n=3$ and 4.[27] These DFT results are inconsistent with the conclusions in the thermochemical and PD studies that the $(CO_2)_n^+$ clusters have the dimer ion core structure, $C_2O_4^+ \cdots (CO_2)_{n-2}$. However, unambiguous explanation for this contradiction has not been given so far.

In this paper, we report IRPD spectroscopy of $(CO_2)_n^+$ with $n=3-8$ in the 1000–3800 cm^{-1} region. There are two problems to be solved for $(CO_2)_n^+$ from the IRPD spectra: One is to address the two proposed models for understanding the spectroscopy: the CO_2^+ core structure and the completely charge-delocalized structure for the $(CO_2)_n^+$ clusters. Since the IR band frequency of CO_2^+ is known from the previous IR studies, we can demonstrate if there is a CO_2^+ monomer ion core in $(CO_2)_n^+$. The other is to determine the structure of the $C_2O_4^+$ ion core of the $(CO_2)_n^+$ clusters. Once an IR spectrum of the $C_2O_4^+$ ion core is obtained by IRPD spectroscopy, one

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can discuss the structure with the aid of quantum chemical calculations. It has been demonstrated that in the IR spectroscopic study of $(CS_2)_n^+$, the solvation substantially affects the structure of the ion core, even in rare-gas matrices.[28] Therefore, the observation of IRPD spectra as a function of the cluster size is essential to understand the relationship between the structure of the ion core and solvation features.

II. EXPERIMENTAL AND COMPUTATIONAL

The details of our experiment have been given elsewhere.[28] Briefly, pure CO_2 gas is injected into a source chamber through a pulsed nozzle with a stagnation pressure of 0.2 MPa. The pulsed free jet crosses an electron beam at the exit of the nozzle, producing $(CO_2)_n^+$. The cluster ions produced are accelerated into a flight tube. 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 the 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 PD laser. IRPD spectra of parent ions are obtained by plotting normalized yields of fragment ions against wavenumber of the IR laser. Fragmentation channel detected for the IRPD spectra of $(CO_2)_n^+$ is mainly the loss of one CO_2 molecule.

The tunable IR light in the 2000–3800 cm^{-1} region is an idler output of an optical parametric oscillator (OPO) (LaserVision). For the IR laser in the 1000–2000 cm^{-1} region, difference frequency generation (DFG) is obtained by mixing a signal and an idler output of the OPO laser with an $AgGaSe_2$ crystal. The DFG output is introduced to the vacuum chamber after removing the signal and idler outputs with a ZnSe filter. The output energy is 0.2–1 mJ/pulse in the 1100–2000 cm^{-1} region and 0.1–5 mJ/pulse in the 2000–3800 cm^{-1} region.

In order to analyze the IRPD spectra, we carry out quantum chemical calculations of $(CO_2)_n^+$ with $n=2-6$ with the GAUSSIAN03 program package.[29] Geometry optimization and vibrational analysis are done at the MP2/6-311+G* and B3LYP/6-311+G* levels. No scaling factor is employed for the vibrational frequencies calculated.

III. RESULTS AND DISCUSSION

A. IRPD spectra of $(CO_2)_n^+$

Figure 1 shows the IRPD spectra of $(CO_2)_n^+$ ($n=3-8$) in the 1000–3800 cm^{-1} region. All the spectra exhibit a few strong bands in the 2000–2500 cm^{-1} region. In addition to them, there are several weak bands in the 1200–1500 and 3200–3800 cm^{-1} regions. The band positions and widths [full width at half maximum (FWHM)] of the IRPD spectra are collected in Table I. Figure 2 displays expanded views of the IRPD spectra in the 2000–2500 cm^{-1} region. All the spectra in Fig. 2 exhibit sharp bands at ~2350 cm^{-1}; for the $n=3$ and 4 ions, the bands are reproduced by two sharp components. In the 2050–2250 cm^{-1} region, the number of the IRPD bands changes alternately with an increase in the cluster size. The $n=3$ and 5 ions show two bands, while the $n=4$ and 6 ions have only one band in the 2050–2250 cm^{-1} region; the $(CO_2)_n^+$ clusters of $n=6-8$ exhibit one band at ~2145 cm^{-1}. As to the width, the bands of the $n=3$ and 4 ions in the 2050–2250 cm^{-1} region are narrower than 21 cm^{-1}, while the $(CO_2)_n^+$ ions with $n \geq 5$ have relatively broader features (≥ 25 cm^{-1}). Figure 3 displays the IRPD spectra in the 1150–1500 cm^{-1} region. The $n=3$ ion shows four broad bands at 1214, 1286, 1323, and 1392 cm^{-1} with a width of ~25 cm^{-1}. In the IRPD spectrum of $n=4$, the band at ~1214 cm^{-1} becomes very weak and only three bands are identified in the same region. The widths of the $n=4$ bands are ~19 cm^{-1}, similar to those of $n=3$. The $n=5$ ion also has three IR bands, but the bandwidths are quite narrower (~10 cm^{-1}) than those of $n=3$ and 4. The intensity of the band at ~1330 cm^{-1} relative to the bands at ~1285 and ~1395 cm^{-1} becomes weaker for $n=5$. For $n=6-8$, the ~1330 cm^{-1} band cannot be observed clearly and only two bands appear at ~1285 and ~1395 cm^{-1} with a bandwidth of ~10 cm^{-1}. The IRPD spectra in the 3200–3800 cm^{-1} region show more complicated features (Fig. 4) as compared to the spectra in the other regions. All the spectra show sharp bands at ~3610 and ~3715 cm^{-1}. Similar to the case of the ~2350 cm^{-1} band, the 3610 and 3715 cm^{-1} bands of $n=3$ and 4 have two sharp components for each band. In addition to the bands in the 3600–3750 cm^{-1} region, the $n=3$ and 4 clusters have several well-resolved bands in the 3200–3500 cm^{-1} region. In contrast, the IRPD spectra of $n=5-8$ show broad features in the same region.

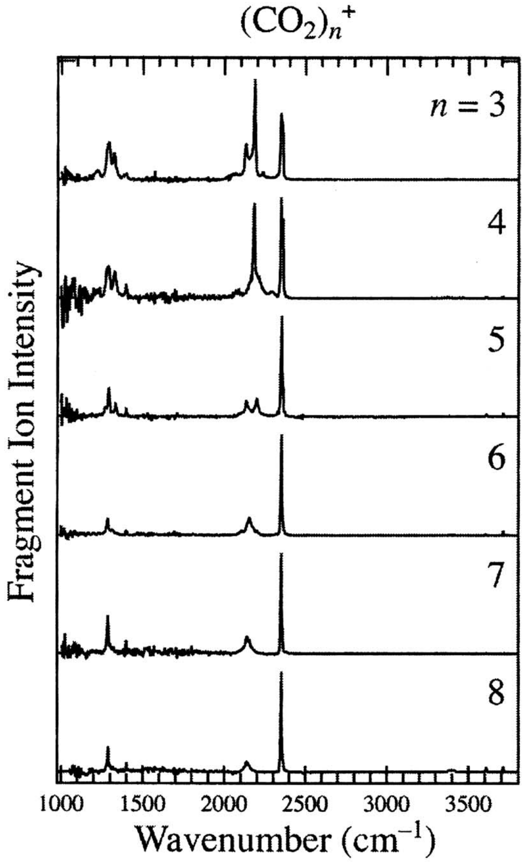


FIG. 1. IRPD spectra of $(CO_2)_n^+$ with $n=3-8$ in the 1000–3800 cm^{-1} region.

On the basis of previous IR studies on CO_2-related spe-

TABLE I. Band position (cm^{-1}), width (FWHM, in parentheses), and assignment of the IRPD spectra of $(CO_2)_n^+$ (n=3–8).

Band position						
n=3	n=4	n=5	n=6	n=7	n=8	Assignment
1214 (31)	···	···	···	···	···	$C_2O_4^+$
1286 (27)	1283 (25)	1290 (11)	1285 (18)	1287 (10)	1288 (9)	CO_2 $(\nu_1, 2\nu_2)$
1323 (19)	1326 (21)	1332 (13)	···	···	···	$C_2O_4^+$
1392 (22)	1395 (11)	1398 (5)	1399 (3)	1399 (–)	1399 (–)	CO_2 $(\nu_1, 2\nu_2)$
2130 (21)	2179 (9)	2136 (30)	2155 (44)	2144 (44)	2140 (35)	$C_2O_4^+$
2184 (10)		2198 (25)				
2347 (13)	2346 (7)	2351 (10)	2351 (7)	2351 (7)	2351 (7)	CO_2 (ν_3)
2356 (6)	2357 (5)					
3263 (10)	3270 (8)	3251 (28)	3399 (58)	3399 (56)	3399 (49)	$C_2O_4^+$
3294 (28)	3300 (27)	3386 (87)				
3367 (20)	···	3495 (27)				
3379 (12)	3373 (30)					
3415 (10)	···					
3446 (16)	3440 (16)					
3474 (10)	3467 (12)					
3595 (12)	3601 (7)	3610 (8)	3610 (7)	3610 (6)	3610 (6)	CO_2 $(\nu_1+\nu_3, 2\nu_2+\nu_3)$
3611 (8)	3611 (6)					
3701 (14)	3705 (9)	3713 (9)	3713 (7)	3713 (6)	3713 (5)	CO_2 $(\nu_1+\nu_3, 2\nu_2+\nu_3)$
3715 (8)	3713 (7)					

cies, one can assign several bands in the IRPD spectra. First, the strong bands at ~2350 cm^{-1} (Fig. 2) can be assigned to the antisymmetric CO stretching vibration (ν_3) of solvent CO_2 molecules because neutral CO_2 shows the band at 2349.3 cm^{-1}.[30] For the n=3 and 4 ions, the bands at ~2350 cm^{-1} are reproduced by two components. These components may be attributed to solvent CO_2 molecules that are bonded to different positions of an ion core. For gaseous CO_2, the Fermi resonance between ν_1 and $2\nu_2$ leads to two Raman bands at 1285.5 and 1388.3 cm^{-1}.[30] Although these vibrations are IR inactive under the isolated condition, they appear at 1284.3 and 1376 cm^{-1} in IR spectra of CO_2 in solid Ne.[22] Similarly, all the IR spectra in Fig. 3 display bands at ~1285 and ~1395 cm^{-1}; these frequencies are close to the positions of the Fermi doublet of CO_2. These bands increase the intensities relative to the band at ~1330 cm^{-1}, which corresponds to $C_2O_4^+$, with an increase in the number of solvent molecules. Therefore, it is reasonable that the bands at ~1285 and ~1395 cm^{-1} are assigned to the Fermi doublet of solvent CO_2 molecules. The bands at ~3610 and ~3715 cm^{-1} (Fig. 4) are also ascribed to the transition of solvent CO_2 molecules because gaseous CO_2 shows IR bands at 3609 and 3716 cm^{-1}.[30] These are attributed to the combination bands, i.e., $(2\nu_2+\nu_3)$ and $(\nu_1+\nu_3)$.

The IR bands other than those mentioned above cannot be explained by the vibrations of neutral CO_2. These bands are due to the ion core in the $(CO_2)_n^+$ cluster ions. The CO_2^+ monomer ion displays the IR band of ν_3 at ~1423 cm^{-1}.[20–23] In the IRPD spectra, however, one cannot find any band at ~1423 cm^{-1} (Fig. 3). Thus, there is no CO_2^+ ion core in the $(CO_2)_n^+$ clusters produced in our experiment. In solid Ne, the $C_2O_4^+$ ion shows an IR band at ~2131 cm^{-1}.[22,23] On the basis of this band position, the bands in the 2100–2200 cm^{-1} region (Fig. 2) can be assigned to the $C_2O_4^+$ ion core. The IR bands of the $C_2O_4^+$ ion core appear at

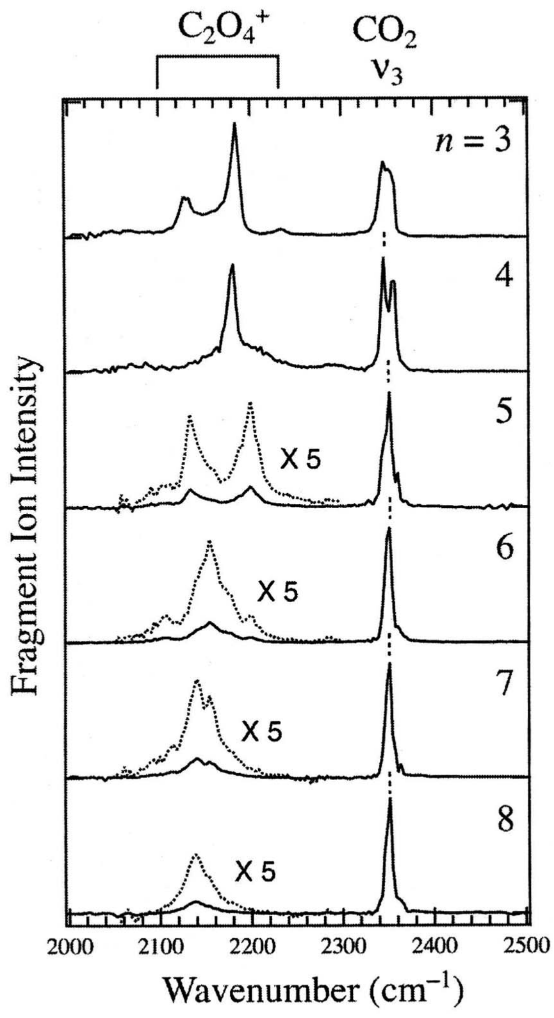


FIG. 2. Expanded views of the IRPD spectra of $(CO_2)_n^+$ with n=3–8 in the 2000–2500 cm^{-1} region. Intensity of the fragment ion for each spectrum is normalized with the maximum value in this region.

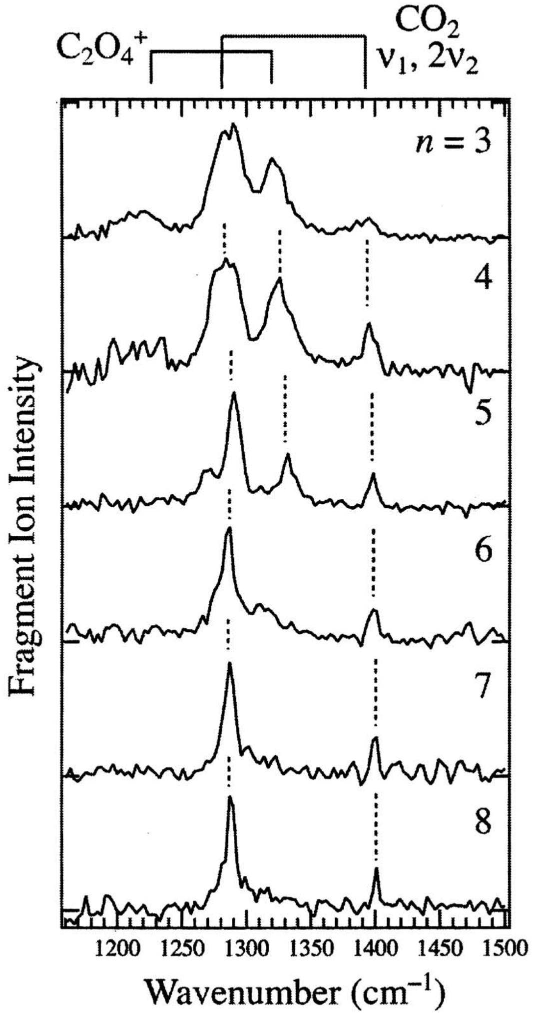


FIG. 3. Expanded views of the IRPD spectra of $(CO_2)_n^+$ with $n=3-8$ in the 1150–1500 cm^{-1} region. Intensity of the fragment ion for each spectrum is normalized with the maximum value in this region.

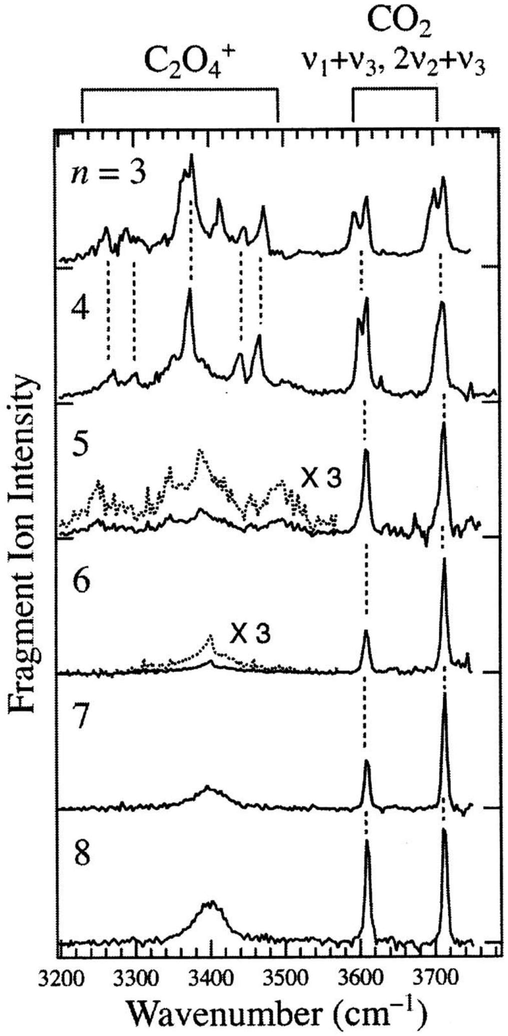
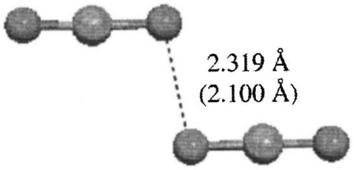


FIG. 4. Expanded views of the IRPD spectra of $(CO_2)_n^+$ with $n=3-8$ in the 3200–3750 cm^{-1} region. Intensity of the fragment ion for each spectrum is normalized with the maximum value in this region.

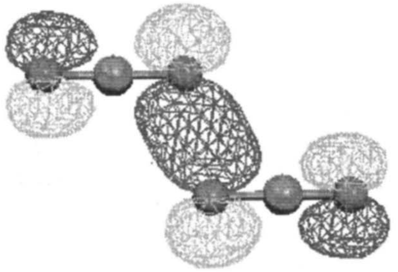
a frequency slightly lower than that of solvent CO_2 molecules (~2350 cm^{-1}). Similarly, since the bands in the 3200–3500 cm^{-1} region (Fig. 4) are located on the lower-frequency side of the combination bands of solvent CO_2 molecules, they can be ascribed to combination bands of $C_2O_4^+$. The bands at ~1330 and ~1214 cm^{-1} in Fig. 3 are also unidentified on the basis of the IR studies of neutral CO_2. The $C_2O_4^+$ ion in solid Ne shows an IR band at ~1275 cm^{-1}.[22,23] In addition, since the intensity of the ~1330 cm^{-1} band relative to that of the bands of solvent CO_2 molecules at ~1285 and ~1395 cm^{-1} decreases with an increase in the cluster size, this band can be attributed to the $C_2O_4^+$ ion core of $(CO_2)_n^+$. The 1214 cm^{-1} component in the IR spectrum of $(CO_2)_3^+$ may also be due to the $C_2O_4^+$ ion core because its intensity also becomes quite weaker with an increase in the cluster size. The structure of the $C_2O_4^+$ ion core is discussed in Secs. III B and III C and with the aid of quantum chemical calculations.

B. Quantum chemical calculations of $C_2O_4^+$

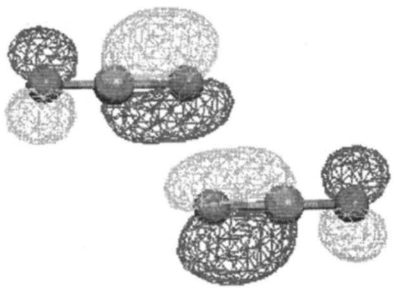
Figure 5(a) shows the optimized structure of $C_2O_4^+$, and only one stable isomer (2A) is obtained at both the B3LYP/6-311+G* and MP2/6-311+G* levels. Isomer 2A has a C_{2h} structure, and the positive charge is delocalized over the constituent molecules. Contrary to the case of $C_2S_4^+$, there is no isomer with C_2 symmetry for $C_2O_4^+$.[28] The distances between the oxygen atoms of the two CO_2 molecules in isomer 2A are 2.319 and 2.100 Å at the B3LYP/6-311+G* and MP2/6-311+G* levels, respectively. These distances are quite shorter than the intermolecular S···S distance of the $C_2S_4^+$ isomer with C_2 symmetry (2.955 Å) calculated at the B3LYP/6-311+G* level.[28] Figures 5(b) and 5(c) display the highest occupied molecular orbital (MO) (21β) and the lowest unoccupied MO (22β) for beta electron of isomer 2A calculated at the UMP2/6-311+G* level (in the unrestricted calculation, there are 22 alpha electrons and 21 beta electrons for $C_2O_4^+$). As a result of the CR interaction, the intermolecular bonding MO is formed (21β) for isomer 2A. The CR transition observed in the visible region is due to the electron promotion from 21β to 22β.[14–18] Results of vibrational analysis for isomer 2A are collected in Table II. The right column shows the assignment of normal modes of isomer 2A. The normal modes are categorized with intramolecular motions of constituent CO_2 molecules. The



(a) 2A (C_{2h})

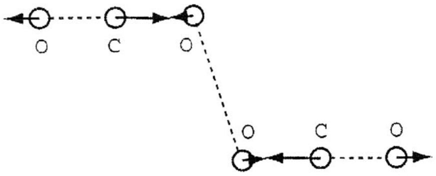


(b) 21β MO

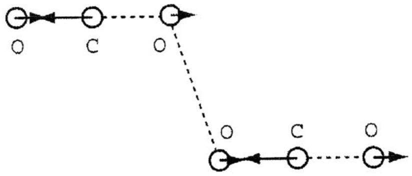


(c) 22β MO

FIG. 5. (a) Optimized structure of $C_2O_4^+$ (isomer 2A). [(b) (c)] The highest occupied MO (21β) and the lowest unoccupied MO (22β) of isomer 2A for β electron calculated at the UMP2/6-311+G* level.



(a) $11a_g$



(b) $12b_u$

FIG. 6. Normal modes of isomer 2A with the antisymmetric CO stretching vibration in the CO_2 components.

CO_2 components in isomer 2A have almost a linear structure, similar to neutral CO_2. The normal modes of isomer 2A are composed of intramolecular motions of the CO_2 components except for the four low-frequency intermolecular modes. Figure 6 shows schematic drawings of the highest-frequency ($12b_u$) and the second highest-frequency ($11a_g$) modes of the $C_2O_4^+$ ion. For these vibrational modes, each of the CO_2 components shows the antisymmetric CO stretching vibration. The in-phase and out-of-phase combinations of these vibrations produce the $11a_g$ and $12b_u$ normal modes; only the nontotally symmetric mode ($12b_u$) is IR active in C_{2h} symmetry.

Here we have to mention that the vibrational analysis done at the MP2/6-311+G* level provides anomalous values for the frequency and the IR intensity (see Table II). Some of the normal modes have IR intensities higher than 10000 km/mol, which are unlikely on the basis of the value calculated for the ν_3 mode of neutral CO_2 (604 km/mol). The highest frequency of isomer 2A at the MP2 level (3879 cm^{-1}) seems to be too high for the $C_2O_4^+$ system. Comparing the results of the vibrational analysis with the B3LYP and the MP2 methods in detail, one can find that the MP2 calculations overestimate force constants of the normal modes, while reduced masses and normal coordinates are comparable between the

TABLE II. Vibrational frequency (cm^{-1}), IR intensity (km/mol), and irreducible representation of isomer 2A calculated at the B3LYP/6-311+G* and MP2/6-311+G* levels.

B3LYP		MP2		
Frequency	IR intensity	Frequency	IR intensity	Assignment[a]
39	0 (a_u)	36	0 (a_u)	(Intermolecular vibrations)
63	1 (b_u)	126	0 (a_g)	(Intermolecular vibrations)
89	0 (a_g)	129	160 (b_u)	(Intermolecular vibrations)
228	0 (a_g)	359	0 (a_g)	(Intermolecular vibrations)
598	44 (b_u)	601	0 (b_g)	OCO bending
614	0 (b_g)	601	54 (a_u)	OCO bending
614	0 (a_g)	648	0 (a_g)	OCO bending
617	69 (a_u)	715	2885 (b_u)	OCO bending
1324	0 (a_g)	1266	0 (a_g)	Sym. CO stretching
1328	78 (b_u)	1472	13434 (b_u)	Sym. CO stretching
2090	0 (a_g)	2473	0 (a_g)	Antisym. CO stretching
2143	311 (b_u)	3879	670020 (b_u)	Antisym. CO stretching

[a] These assignments describe intramolecular motions of the constituent CO_2 molecules of isomer 2A. The normal modes of isomer 2A are recognized as linear combinations of these intramolecular motions.

B3LYP and the MP2 results. This overestimation of the force constants results in the unphysical values of the vibrational frequencies in the MP2 calculations. These anomalous IR intensities and frequencies may probably be a consequence of symmetry breaking effects occurring in the single-reference methods, such as the Hartree–Fock and the MP2 calculations.[31–36] Symmetry breaking effects sometimes predict unreasonably lower-symmetry structures, spurious dipole moments, and unreliable IR intensities and vibrational frequencies. In contrast, since DFT includes electron correlation effects during the optimization of the Kohn–Sham orbitals, the DFT calculations of the $C_2O_4^+$ ion in this study can avoid the difficulty due to symmetry breaking effects and provide more meaningful results.[36] Supporting information on the calculated results of $(CO_2)_n^+$ is available in our EPAPS file.[37]

C. Structure of $(CO_2)_3^+$

For the determination of the structure of $(CO_2)_n^+$, it is most reliable to examine the IR spectra in the antisymmetric CO stretching region ($2000-2500\ cm^{-1}$) because only the fundamental vibrations will appear in this region.[30] The IRPD spectrum of $(CO_2)_3^+$ shows the bands due to the solvent CO_2 molecule at $\sim 2350\ cm^{-1}$ and the $C_2O_4^+$ ion at around $2150\ cm^{-1}$, implying the $C_2O_4^+$ core structure, $C_2O_4^+ \cdots CO_2$. Attachment of one CO_2 molecule to the $C_2O_4^+$ ion reduces the symmetry of the cluster from C_{2h} to C_2 or lower symmetry. This symmetry reduction results in the appearance of two IR bands of the $C_2O_4^+$ core in the $2000-2300\ cm^{-1}$ region because the totally symmetric vibration [$11a_g$ in Fig. 6(a)], which is IR inactive in C_{2h} symmetry, gains some IR intensity.[28] Therefore, the IR bands at 2130 and $2184\ cm^{-1}$ in the IRPD spectrum of $(CO_2)_3^+$ (Fig. 2) are assigned to the in-phase and out-of-phase combinations of the antisymmetric CO stretching vibrations of the two CO_2 components in the $C_2O_4^+$ ion core.

The geometry optimization of $(CO_2)_3^+$ done at the B3LYP/6-311+G* and the MP2/6-311+G* levels provides nine stable isomers (the details of the calculated results are described in the EPAPS file).[37] Among them, three isomers satisfy the experimental suggestion that the $(CO_2)_3^+$ ion has the $C_2O_4^+$ ion core. Figure 7 shows the structures of the three isomers (3A–3C) of $(CO_2)_3^+$. All the three isomers are obtained using the MP2 method. The most stable structure is isomer 3A, in which the neutral CO_2 molecule is located along the C_2 axis. In isomer 3B, the solvent CO_2 molecule is situated in the plane of the ion core. In isomer 3C, the oxygen atom of the solvent CO_2 molecule is on the C_2 axis of the ion core, but its molecular axis is perpendicular to the C_2 axis. For isomer 3A, the structure of the $C_2O_4^+$ ion core is largely distorted from C_{2h} to C_2 symmetry, whereas isomers 3B and 3C have a planar, C_{2h}-like $C_2O_4^+$ ion core. One of the straightforward ways to identify the structure of $(CO_2)_3^+$ among these isomers is the comparison of the IRPD spectrum of $(CO_2)_3^+$ with the IR spectra calculated for these isomers. However, the vibrational analysis of isomers 3A–3C with the MP2 method also provides anomalous IR intensities and vibrational frequencies, which may be due to symmetry breaking effects. Therefore, it is not possible at present to give a decisive conclusion on the structure of $(CO_2)_3^+$ based on the vibrational analysis for isomers 3A–3C. On the basis of the consideration of the symmetry lowering, all isomers 3A–3C can meet the condition of the IRPD spectrum of $(CO_2)_3^+$; there are two bands at 2130 and $2184\ cm^{-1}$. Among the isomers in Fig. 7, the most stable structure is isomer 3A. Therefore, we can propose that the structure of the $(CO_2)_3^+$ ion is ascribed to isomer 3A (this assignment is supported by the preliminary vibrational analysis for isomers 3A–3C, which is described in the EPAPS file).[37] The determination of the temperature of $(CO_2)_3^+$ with metastable decay rates and the examination of the temperature dependence of the IRPD spectral feature will give important information on the contributions of multiple isomers to the IRPD spectra, which is our future work. In isomer 3A the solvent CO_2 molecule, which is bound to the $C_2O_4^+$ ion core with the molecular axis pointed to the intermolecular semicovalent bond, changes the structure of the $C_2O_4^+$ ion core into the C_2 structure. In contrast, in isomer 3B the solvent molecule, which is located in the same plane of the C_{2h} $C_2O_4^+$ ion core, does not distort the planar structure of the ion core. These solvation features in 3A and 3B rationalize the development of the structure of $(CO_2)_n^+$ for $n \geq 4$.

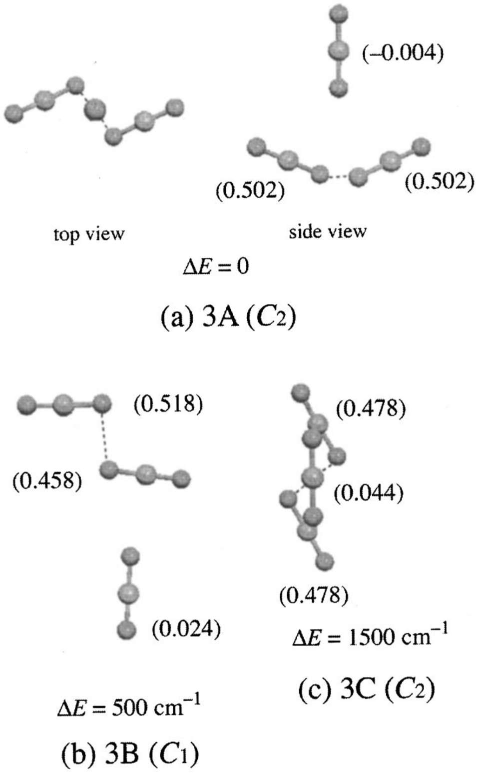


FIG. 7. Optimized structures of $(CO_2)_3^+$ calculated at the MP2/6-311+G* level. Numbers in parentheses represent the positive charge distribution on the constituent CO_2 molecules.

D. Structural development for $(CO_2)_n^+$ with $n \geq 4$

Based on the large structural change of the $C_2O_4^+$ core from isomer 2A to 3A, it is quite probable that the solvation of further CO_2 molecules will also affect the $C_2O_4^+$ structure.

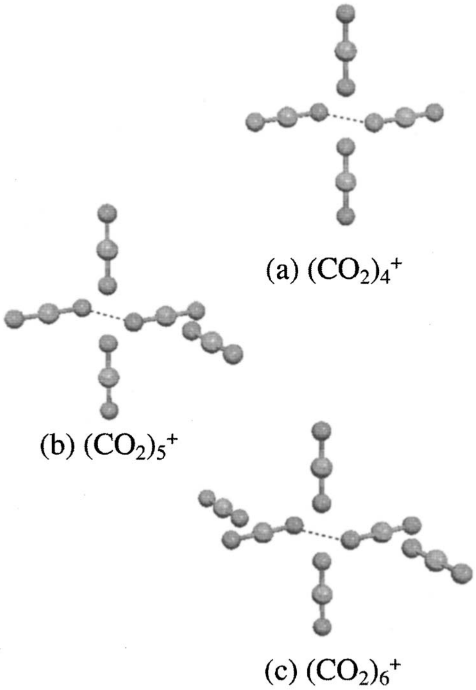


FIG. 8. Schematic drawings of structures for $(CO_2)_n^+$ (n=4–6) proposed on the basis of the IRPD spectra.

A sign of this structural change in larger clusters is found in the IRPD spectra in the 2000–2300 cm^{-1} region (Fig. 2). As mentioned above, the number of the IRPD band in the 2000–2300 cm^{-1} alternately changes between two (n=3 and 5) and one (n=4 and 6). This change in the number of the IR band of $C_2O_4^+$ reflects the alternation of the symmetry of the clusters. The C_{2h} structure of bare $C_2O_4^+$ shows only one band in the 2000–2300 cm^{-1} region. For $(CO_2)_3^+$, one solvent CO_2 molecule changes the symmetry of the $C_2O_4^+$ core from C_{2h} to C_2, leading to two IR bands. Therefore, the appearance of only one band for $(CO_2)_4^+$ suggests a C_{2h} form. As seen in isomer 3A, the most probable type of the solvation to the $C_2O_4^+$ ion core is the perpendicular way; a solvent CO_2 molecule points the molecular axis to the middle of the intermolecular bond of $C_2O_4^+$, perpendicularly to the $C_2O_4^+$ plane. In the case of $(CO_2)_3^+$, since there is only one CO_2 molecule attached, the planar structure of the $C_2O_4^+$ core is largely distorted by the solvation. For the $(CO_2)_4^+$ ion, two solvent CO_2 molecules are probably located on opposite sides of the $C_2O_4^+$ ion core, keeping the plane of $C_2O_4^+$. Figure 8(a) shows a proposed structure of $(CO_2)_4^+$. Solvation of the third CO_2 molecule will reduce the symmetry of the $(CO_2)_5^+$ ion lower than C_{2h}. Since the most preferable solvation sites of the $C_2O_4^+$ ion core are already occupied by the first and the second CO_2 molecules, the third solvent molecule has to find another solvation site. As demonstrated in the calculations of $(CO_2)_3^+$ (Fig. 7), the second most probable way of the solvation to the $C_2O_4^+$ ion core is the isomer 3B type, in which the solvent molecule is situated in the plane of a planar $C_2O_4^+$ ion. For the $(CO_2)_6^+$ ion, the IRPD spectrum has only one band of the $C_2O_4^+$ ion core in the 2000–2300 cm^{-1} region, demonstrating that the n=6 cluster regains C_{2h} symmetry. The fourth solvent molecule is probably located on the opposite side of the third molecule in the plane of the $C_2O_4^+$ ion core; this solvation makes the $(CO_2)_6^+$ cluster C_{2h} symmetry again. Proposed structures of $(CO_2)_5^+$ and $(CO_2)_6^+$ are displayed in Figs. 8(b) and 8(c). For the $(CO_2)_n^+$ clusters with n=7 and 8, only one band appears in the 2000–2300 cm^{-1} region. This is probably because the first solvation shell is full in $(CO_2)_6^+$, and further solvent molecules are bonded outside of the first shell. As a result, the ion core feels the effective symmetry of C_{2h} in the n=7 and 8 clusters. It is our future work to reproduce the alternation of the IRPD spectra by quantum chemical calculations.

Engelking[9] estimated the binding energy of one CO_2 molecule within the $(CO_2)_n^+$ (n=4–13) clusters with a statistical model from measurements of cluster evaporation lifetime and average kinetic energy release. The binding energy of one CO_2 molecule in the $(CO_2)_4^+$ ion was determined to be ~200 meV, which corresponds to ~1610 cm^{-1}. For n=5–8, the binding energy becomes 156±26 meV (~1260±210 cm^{-1}), which is much smaller than that of n=4. Johnson *et al.*[16] reported in their study on visible PD of $(CO_2)_n^+$ (n=2–10) that the PD cross section at 1064 nm largely decreases between n=3 and 4 and shows similar values for $n \geq 4$. They suggested that since the absorption at 1064 nm corresponds to the CR transition of the $C_2O_4^+$ ion, from the bound to the repulsive potential curves at large intermolecular distance, the alternation of the cross section for cluster size reflects the distortion of the $C_2O_4^+$ ion core by solvation. Combining the results of the binding energy[9] and the PD at 1064 nm[16] to our IRPD results, we come to the following conclusions: (1) Primarily, the solvation of the first and the second CO_2 molecules to the $C_2O_4^+$ ion core changes extensively both the electronic and geometric structures of the ion core as detected in PD spectroscopy at 1064 nm and IRPD spectroscopy in the region of 2000–2300 cm^{-1}; (2) the interaction of the third and the fourth solvent molecules with the $C_2O_4^+$ ion core is weaker than that of the first and the second molecules and does not distort the planar structure of the $C_2O_4^+$ ion core;[16] (3) from the viewpoint of IR spectroscopy, the weaker interaction of the third and the fourth solvent molecules causes the noticeable change in the IRPD spectra for n=5 and 6; (4) since the fifth and sixth solvent molecules are not bonded directly to the $C_2O_4^+$ ion core, the interaction with the ion core is too weak to be detected even by IR spectroscopy. These conclusions demonstrate quite high sensitivity of IR spectroscopy to the cluster structure.

Evidence of the structural development for $(CO_2)_n^+$ can also be seen in the bandwidth of the IRPD spectra. The IRPD spectra in the 1150–1500 cm^{-1} region (Fig. 3) show that the bandwidth is larger for n=3 and 4 relative to that for n=5–8. In addition, the bands of n=3 and 4 seem to have Gaussian-type shapes, whereas the other bands show Lorentzian shapes. In the region higher than 1600 cm^{-1}, however, the n=3 and 4 ions exhibit Lorentzian band shapes. From these findings, relatively warmer ensembles may probably be responsible for the IRPD bands in the 1150–1500 cm^{-1} region for the n=3 and 4 ions. This consideration is reasonably supported by the results of the binding energy of $(CO_2)_n^+$; the binding energy of one CO_2 molecule in the $(CO_2)_4^+$ ion is ~1610 cm^{-1}, whereas those of n=5–8 are ~1260 cm^{-1}.[9]

On the other hand, colder ensembles of the $n=3$ and 4 ions can be dissociated by the absorption of the IR light higher than ~1610 cm^{-1}. For the $n=5-8$ clusters, the IR light can probably dissociate cold clusters in almost the whole IR region of the present study.

The other issue concerning the bandwidth of the IRPD spectra is that some of the IR bands show broad features for the $n=5-8$ clusters. As can be seen in Fig. 2, the $C_2O_4^+$ ion core of $n=3$ and 4 shows the IRPD band(s) around 2150 cm^{-1} with a bandwidth of ~15 cm^{-1}. In contrast, the width of the $C_2O_4^+$ bands for $n=5-8$ is approximately 36 cm^{-1}, more than two times wider than that of $n=3$ and 4. On the other hand, the antisymmetric CO stretching bands of solvent CO_2 molecules at ~2350 cm^{-1} show a quite narrow width of ~8 cm^{-1} for all the clusters. A similar trend is seen for the combination bands in the 3200–3800 cm^{-1} region (Fig. 4). The IRPD spectra of $n=3$ and 4 in the 3200–3500 region, which are ascribed to the combination bands of the $C_2O_4^+$ ion core, exhibit congested but well-resolved band features. However, the spectra of $n=5-8$ in the same region show quite broad bands. Similar to the case of the antisymmetric CO stretching vibration around 2350 cm^{-1}, the combination bands of solvent CO_2 molecules at ~3610 and ~3715 cm^{-1} are quite narrow with a bandwidth of ~8 cm^{-1}. Different from the case in the 1150–1500 cm^{-1} region, therefore, these results can be ascribed not to the cluster binding energy or the cluster temperature but to the mode-dependent lifetime of the excited vibrational states. Since only the IR bands of the $C_2O_4^+$ ion core at ~2150 and ~3400 cm^{-1} are relatively broad for the $n=5-8$ clusters, some relaxation channels will open only for the vibrations of the $C_2O_4^+$ ion core from $n=5$. As mentioned above, the $(CO_2)_n^+$ ions with $n \geq 5$ have solvent CO_2 molecules in the plane of the $C_2O_4^+$ ion. The vibrations of the $C_2O_4^+$ ion core observed in the IRPD spectra are related to CO stretching vibrations, which are recognized as in-plane motions of the $C_2O_4^+$ ion. Therefore, the vibrations of the $C_2O_4^+$ ion in the $(CO_2)_n^+$ ($n \geq 5$) clusters can be coupled well with intermolecular vibrations that appear due to solvation of CO_2 molecules in the plane of the ion core. The origin of the broadening of the $C_2O_4^+$ bands for $n \geq 5$ is ascribed to shorter lifetimes of the vibrational levels by intracluster vibrational energy redistribution. From the bandwidth of the $C_2O_4^+$ bands for $n=5-8$ (36 cm^{-1}), a lower limit of the lifetime of the vibrationally excited states of the $C_2O_4^+$ ion core is estimated to be ~15 ps.

IV. SUMMARY

The IRPD spectra of $(CO_2)_n^+$ with $n=3-8$ have been measured in the 1000–3800 cm^{-1} region. Since the spectra show IR bands assignable to solvent CO_2 molecules but not to the CO_2^+ monomer ion, it is confirmed that the $(CO_2)_n^+$ clusters have the dimer ion core structure, $C_2O_4^+ \cdots (CO_2)_{n-2}$. The IRPD spectra display spectral features strongly dependent on the cluster size, different from the case of $(CS_2)_n^+$.[28] According to the results of quantum chemical calculations of $(CO_2)_n^+$ and the dependence of the IRPD spectral features on the cluster size, we deduce the following structural development for $(CO_2)_n^+$: Quantum chemical calculations for bare $C_2O_4^+$ ion predict a planar C_{2h} structure. Attachment of solvent CO_2 molecules to $C_2O_4^+$ changes the structure of the $C_2O_4^+$ ion to the C_2 form ($n=3$) and to the C_{2h} one ($n=4$). These findings demonstrate a floppy character of the planar $C_2O_4^+$ ion under the effect of solvent molecules attached out of the plane. The third and fourth solvent CO_2 molecules are located in the plane of the $C_2O_4^+$ ion core in the $n=5$ and 6 clusters; these solvent molecules do not significantly affect the planar $C_2O_4^+$ core structure. The first solvation shell of the $C_2O_4^+$ ion is fully occupied by four CO_2 molecules ($n=6$).

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