# Ion core structure in $(CS_2)_n^+$ and $(CS_2)_n^-$ ($n=3-10$) studied by infrared photodissociation spectroscopy

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Infrared photodissociation spectra of $(CS_2)_n^+$ and $(CS_2)_n^-$ with $n=3-10$ are measured in the $1100-2000$ cm$^{-1}$ region. All the $(CS_2)_n^+$ clusters exhibit three bands at $\sim 1410$, $\sim 1490$, and $\sim 1540$ cm$^{-1}$. The intensity of the 1540 cm$^{-1}$ band relative to those of the other bands increases with increasing the cluster size, indicating that the band at 1540 cm$^{-1}$ is assignable to the antisymmetric CS stretching vibration of solvent $CS_2$ molecules in the clusters. On the basis of density functional theory calculations, the 1410 and 1490 cm$^{-1}$ bands of $(CS_2)_n^+$ are assigned to CS stretching vibrations of the $C_2S_4^+$ cation core with a $C_2$ form. The $(CS_2)_n^-$ clusters show two bands at around 1215 and 1530 cm$^{-1}$. Similar to the case of cation clusters, the latter band is ascribed to the antisymmetric CS stretching vibration of solvent $CS_2$ molecules. Vibrational frequency analysis of $CS_2^-$ and $C_2S_4^-$ suggests that the 1215 cm$^{-1}$ band is attributed to the antisymmetric CS stretching vibration of the $CS_2^-$ anion core with a $C_{2v}$ structure. © *2008 American Institute of Physics.*
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## I. INTRODUCTION

One of the fundamental issues for molecular cluster ions is the degree of the charge localization within them. For homomolecular cluster ions, it is frequently seen that the intermolecular charge resonance (CR) interaction occurs in the clusters and provides a symmetrical dimer ion core, in which the positive or negative charge is equally shared by two molecules. When an ion $M^\pm$ and a neutral molecule M form a symmetrical dimer ion $M_2^\pm$, the CR interaction produces two CR states. Wavefunctions of the CR states are described as $\Psi_{CR} = \psi(M_a^\pm) \cdot \psi(M_b) \pm \psi(M_a) \cdot \psi(M_b^\pm)$, where $\psi(M^\pm)$ and $\psi(M)$ stand for wavefunctions of the electronic ground state of a monomer ion and a neutral monomer, respectively. Since the resonance energy of the CR interaction is quite large ($0.1-1$ eV), the binding energy of symmetrical dimer ions is quite larger than those of ion-molecule complexes, and the transition between the CR states appears in the region from near IR (NIR) to visible (vis). Symmetrical dimer ions have been found in studies of high-pressure mass spectroscopy,[1–4] absorption spectroscopy,[5–7] photodissociation (PD) spectroscopy,[8–16] and photoelectron (PE) spectroscopy.[17–21] These experimental methods are quite powerful for examining the CR interaction in cluster ions. On the other hand, these techniques hardly provide detailed information on the geometrical structure of symmetrical dimer ions such as intermolecular orientation of constituent molecules. Mass spectrometric studies basically show only the thermochemical property of cluster ions. Since CR bands are due to the transition from a bound to repulsive CR state, these are essentially broad. Therefore, it is quite difficult to derive information on the structure of symmetrical dimer

ions from absorption or PD spectra in the NIR-vis region. PE bands of cluster anions also show broad features because of large structural difference between anion and neutral states.

For overcoming these difficulties, IR absorption spectroscopy has been applied well to molecular cluster ions.[22–25] IR spectra show useful information on molecular vibrations that are quite sensitive to both the geometric and electronic structures. Comparison of experimental IR spectra with those predicted by quantum chemical calculations for ionic candidates presents conclusive evidence of the existence of symmetrical dimer ions and their structures. IR absorption spectroscopy of molecular ions trapped in low-temperature solid matrices is one of the most productive investigations. However, there are a few disadvantages for IR absorption spectroscopy in solid matrices. One is that it is quite difficult to remove solvent effect completely even for rare gas matrices. The other is that IR bands due to different species (cations, anions, and different cluster size) frequently appear in the same IR spectrum. Infrared photodissociation (IRPD) spectroscopy, which is our approach used in this study, can avoid these disadvantages. By using a mass spectrometer, one can choose a single cluster size and measure its IR spectrum. IRPD spectroscopy has been applied to a variety of systems such as proton-bound clusters, hydrogen-bonded clusters, and metal-containing ions.[26] On the other hand, there are only a few reports to study CR systems with IRPD spectroscopy. Inokuchi and Nishi reported IRPD spectroscopy of benzene cluster cations, $(C_6H_6)_n^+$, and observed an IR band assignable to the CH stretching vibration of the dimer cation core existing in $(C_6H_6)_n^+$.[27] More recently, Shin *et al.* measured the IRPD spectra of carbon dioxide cluster anions $(CO_2)_n^-$ ($n=2-17$) and found IR bands as characteristic of the symmetrical dimer anion core $C_2O_4^-$.[28]

In this paper, our target system is the positively and

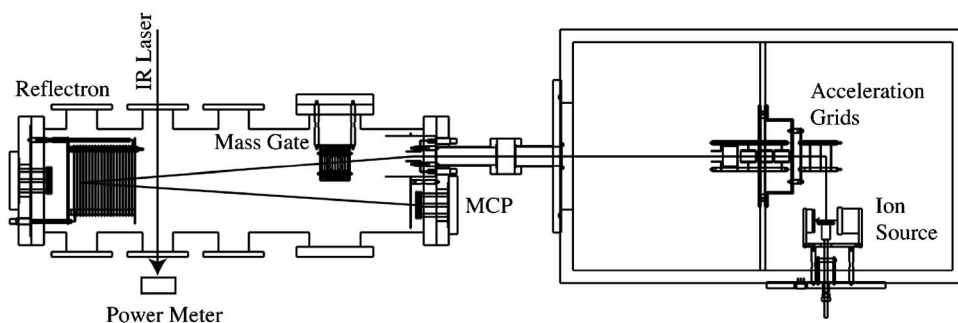a)Author to whom correspondence should be addressed. Electronic mail: y-inokuchi@hiroshima-u.ac.jp.

FIG. 1. Schematic drawing of the mass spectrometer for infrared photodissociation spectroscopy.

negatively charged carbon disulfide clusters, $(CS_2)_n^+$ and $(CS_2)_n^-$. Hiraoka *et al.* studied the thermochemical stability of $(CS_2)_n^+$ and $(CS_2)_n^-$ with a high-pressure mass spectrometer.[29] The intermolecular dissociation energy of $(CS_2)_2^+$ and $(CS_2)_2^-$ was determined to be 24.9 and 21.9 kcal/mol, respectively. On the basis of the results of *ab initio* molecular orbital calculations, they suggested that both the $(CS_2)_2^+$ and $(CS_2)_2^-$ ions have a symmetrical dimer form, $C_2S_4^+$ and $C_2S_4^-$. Zhou and Andrews reported IR spectroscopy of $CS_2^-$, $CS_2^+$, and $C_2S_4^+$ in solid Ne and Ar.[30] They measured IR spectra in the CS stretching region, and found an IR band of the $C_2S_4^+$ cation at $\sim 1380$ cm$^{-1}$. More recently, Yu *et al.* observed an IR band of the $C_2S_4^-$ anion at around 910 cm$^{-1}$.[31] For the $(CS_2)_n^+$ cations, there are few reports on spectroscopic studies in the gas phase. In contrast, the $(CS_2)_n^-$ anions have attracted much attention of many groups. Tsukuda *et al.* reported PE spectroscopy of $(CS_2)_n^-$ with $n=1-6$.[32] The PE spectra demonstrate the coexistence of two electronic isomers represented as $CS_2^- \cdots (CS_2)_{n-1}$ and $C_2S_4^- \cdots (CS_2)_{n-2}$. From the relative intensity of the PE bands, they concluded that the dominant isomer of $(CS_2)_n^-$ with $n=3-6$ has a monomer anion core structure, $CS_2^- \cdots (CS_2)_{n-1}$. The electronic and geometric structures of the $C_2S_4^-$ anion have been well examined also by PD spectroscopy,[33] collision-induced dissociation,[34] PE imaging,[35] and quantum chemical calculations.[36–38] However, the conclusions derived in these studies are slightly different from each other, and the structure of $C_2S_4^-$ has been still a controversial issue.

In the present study, we investigate the structure of the ion core in $(CS_2)_n^+$ and $(CS_2)_n^-$ ($n=3-10$) with IRPD spectroscopy. The IRPD spectra are measured in the 1100–2000 cm$^{-1}$ region and provide IR bands of CS stretching vibrations as characteristic of an ion core and solvent molecules. In order to identify IR bands of ion cores, we carry out geometry optimization and vibrational analysis of several ion species at the B3LYP/6-311+G* level. Comparing the IRPD spectra with those calculated and IR results in solid matrices, we discuss the ion core form existing in the $(CS_2)_n^+$ and $(CS_2)_n^-$ clusters.

## II. EXPERIMENTAL AND COMPUTATIONAL

Figure 1 shows a schematic diagram of the mass spectrometer used in this study. $CS_2$ (Nakalai Tesque) is used without further purification. A mixture of gaseous $CS_2$ and Ar is injected into a source chamber through a pulsed nozzle

(General Valve Series 9) with an orifice diameter of 0.8 mm. The stagnation pressure is 0.4 MPa. The pulsed free jet crosses an electron beam at the exit of the nozzle, producing both $(CS_2)_n^+$ and $(CS_2)_n^-$. The electron kinetic energy is 350 eV. Cluster ions produced are accelerated into a flight tube by applying pulsed electric potential ($\sim 1.3$ kV) to Wiley–McLaren type acceleration grids. By changing the polarity of the acceleration potential, we can select cation or anion clusters. In the flight tube, only target parent ions can go through a mass gate.[39] After passing through the gate, mass-selected parent ions are merged with an output of a pulsed IR laser. Resultant fragment ions are mass-analyzed by a home-made reflectron mass spectrometer and detected by a multichannel plate (MCP) (Burle 31373). An output from the MCP is amplified by a commercial amplifier (Stanford Research Systems SR445A) and fed into a digital storage oscilloscope (LeCroy 9310A). A signal averaged by the oscilloscope is transferred to a personal computer through the general purpose interface bus interface. Yields of fragment ions are normalized by the intensity of the 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 fragmentation channel detected for the IRPD spectra of $(CS_2)_n^+$ and $(CS_2)_n^-$ is the loss of one $CS_2$ molecule.

The tunable IR light used in this study is obtained by difference frequency generation (DFG) between a signal and idler outputs of an optical parametric oscillator (OPO) (LaserVision). The OPO laser is pumped by a fundamental output of a Nd:YAG (yttrium aluminum garnet) laser (Spectra Physics GCR250). A AgGaSe$_2$ crystal is used for DFG, and only the DFG output is introduced to the vacuum chamber after removing the signal and idler outputs with a ZnSe filter. The power of the IR laser is measured at the exit window with a laser detector (Ophir 12A-P). The output energy is 0.2–1 mJ/pulse in the 1100–2000 cm$^{-1}$ region.

In order to analyze the IRPD spectra, we also carried out density functional theory (DFT) calculations with GAUSSIAN03 program package.[40] Geometry optimization and vibrational analysis of several $CS_2$ species are done at the B3LYP/6-311+G* level of theory. For comparison of IRPD spectra with the calculated ones, we apply a scaling factor of 0.9880 to vibrational frequencies calculated. This factor is determined so as to reproduce the frequency of the antisymmetric CS stretching vibration of neutral $CS_2$ monomer.[41]
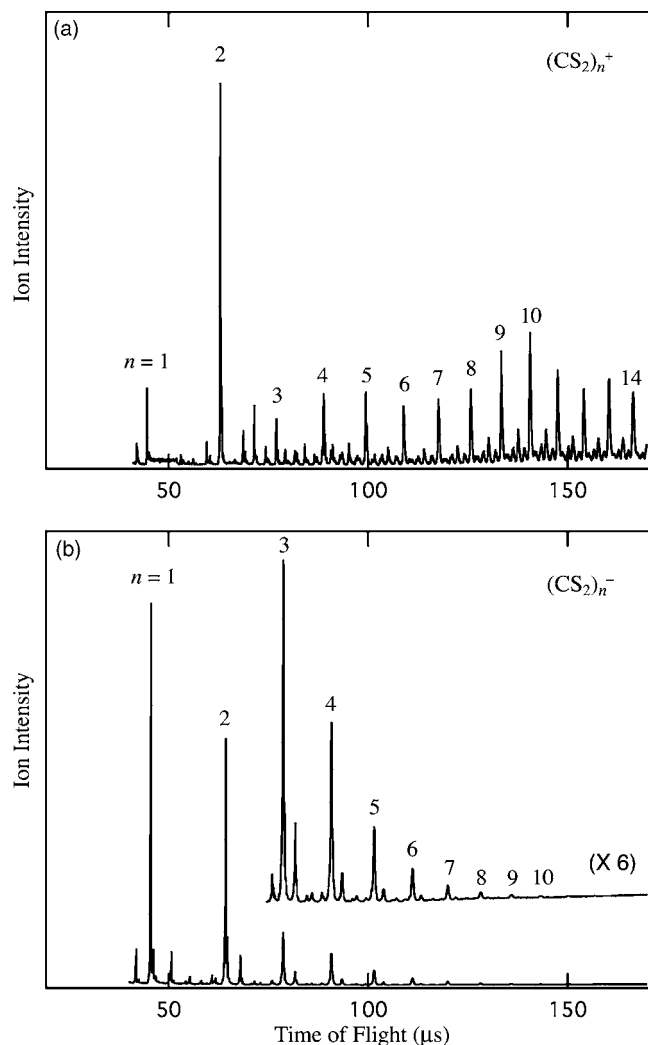
FIG. 2. Time-of-flight mass spectra of (a) $(CS_2)_n^+$ and (b) $(CS_2)_n^-$.



FIG. 3. Infrared photodissociation spectra of (a) $(CS_2)_n^+$ and (b) $(CS_2)_n^-$ with $n=3-10$ in the 1100–2000 cm$^{-1}$ region.

## III. RESULTS AND DISCUSSION

### A. $(CS_2)_n^+$

Figure 2(a) displays a typical example of $(CS_2)_n^+$ mass spectra. Signals of $(CS_2)_n^+$ are clearly observed up to $n=14$, and the strongest one is due to dimer cation $(CS_2)_2^+$. The intensity distribution of the mass spectra is highly dependent on the condition of the mass spectrometer such as electric potential applied to electrostatic ion optics and introduction timing of the ion packet to the flight tube. However, the intensity of the $(CS_2)_2^+$ signal is almost the same as or stronger than that of the monomer cation $CS_2^+$ at all times. This result demonstrates that the $(CS_2)_2^+$ cation probably has a quite stable form. Figure 3(a) shows the IRPD spectra of $(CS_2)_n^+$ ($n=3-10$) in the 1100–2000 cm$^{-1}$ region. The dimer cation $(CS_2)_2^+$ does not photodissociate in this frequency region, implying that the dimer cation has an intermolecular binding energy much larger than those of the higher clusters. Three peaks can be seen at $\sim$1410, $\sim$1490, and $\sim$1540 cm$^{-1}$ for the $(CS_2)_3^+$ cluster. These three bands are also found in the IRPD spectra of clusters larger than $n=3$, but the intensity of the 1540 cm$^{-1}$ band relative to those of the 1410 and 1490 cm$^{-1}$ bands increases with increasing
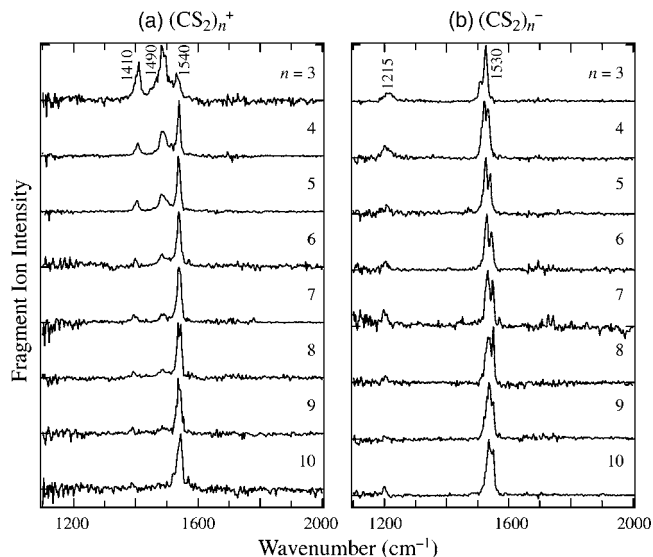
the cluster size. In addition to this tendency, it is known that the antisymmetric CS stretching vibration of neutral $CS_2$ appears at 1535.36 cm$^{-1}$.[41] Thus, the band at $\sim$1540 cm$^{-1}$ can be assigned to the antisymmetric CS stretching vibration of $CS_2$ working as solvent molecules. The 1410 and 1490 cm$^{-1}$ bands are attributed to a cation core in the clusters. The 1540 cm$^{-1}$ band of solvent $CS_2$ stays at almost the same position for all the $(CS_2)_n^+$ ($n=3-10$) clusters. This insensitive property of the CS stretching vibration to the cluster structure represents the difficulty in determining the solvation structure from the IRPD spectra such as hydrogen-bonding systems.[42,43] On the other hand, it is possible to identify constituent species that form a cluster from the CS stretching vibration. The $(CS_2)_3^+$ cation has at least one solvent $CS_2$ molecule because the IRPD spectrum of $(CS_2)_3^+$ exhibits the solvent band at 1540 cm$^{-1}$. Thus, the charge is not delocalized over three molecules, and there is a dimer or monomer cation core in $(CS_2)_3^+$. The position of the ion core bands is almost the same for all the $(CS_2)_n^+$ clusters, indicating that these clusters have a common ion core species. According to the IR results of Zhou and Andrews, the $C_2S_4^+$ cation shows only one peak at 1385.2 cm$^{-1}$ in solid Ne or 1379.7 cm$^{-1}$ in solid Ar.[30] The $CS_2^+$ cation has a band at 1206.8 cm$^{-1}$ in Ne or 1200.5 cm$^{-1}$ in Ar.[30] Since the $(CS_2)_n^+$ ($n=3-10$) clusters show no band at around 1200 cm$^{-1}$ in the IRPD spectra, there is no $CS_2^+$ cation core in $(CS_2)_n^+$. The band position of the cation core part in $(CS_2)_n^+$ ($\sim$1410 and $\sim$1490 cm$^{-1}$) is close to that of $C_2S_4^+$ in solid matrices ($\sim$1380 cm$^{-1}$).[30] Therefore, the 1410 and 1490 cm$^{-1}$ bands in the IRPD spectra of $(CS_2)_n^+$ are due to the $C_2S_4^+$ dimer cation core which exists in the $(CS_2)_n^+$ clusters.

In order to confirm the absence of the $CS_2^+$ cation core and to examine the structure of the $C_2S_4^+$ core, we perform geometry optimization and vibrational analysis for several species concerning $CS_2$. Figures 4(a) and 4(b) show the optimized structures of neutral $CS_2$ and $CS_2^+$ cation. Both $CS_2$ and $CS_2^+$ have a linear structure, and the C–S distance is almost the same with each other ($\sim$1.56 Å). Table I shows
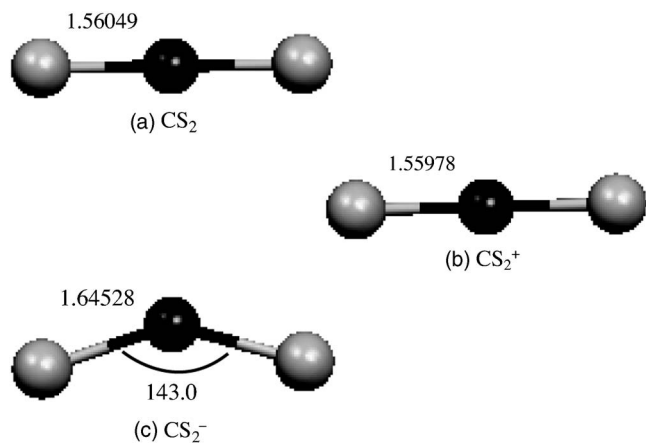
FIG. 4. Optimized structures of (a) $CS_2$, (b) $CS_2^+$, and (c) $CS_2^-$ calculated at the B3LYP/6-311+G* level of theory. Numbers in the figure show the C–S distance and the S–C–S angle.
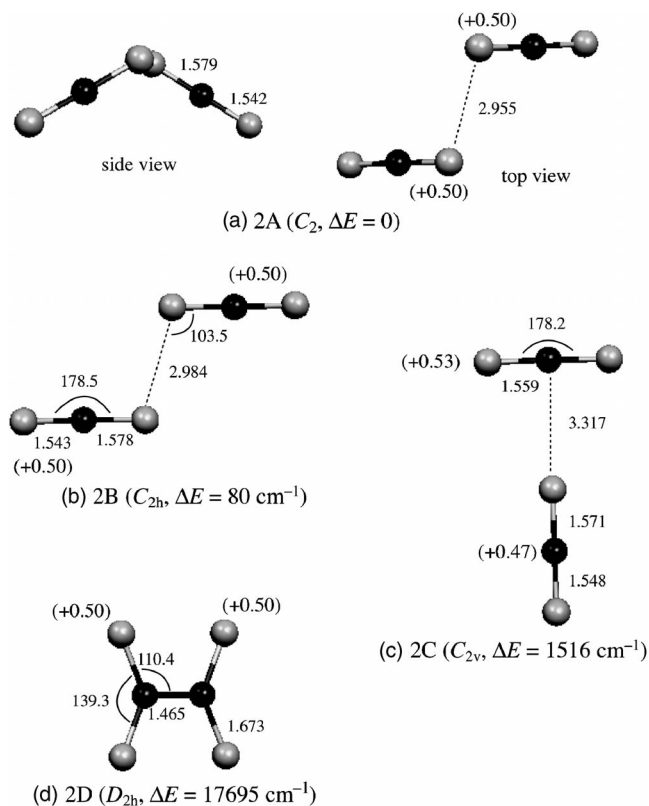


FIG. 5. Optimized structures of the $C_2S_4^+$ cation calculated at the B3LYP/6-311+G* level of theory. Both the side and top views are shown only for 2A. Numbers in the figure show the interatomic distance and the bond angle. $\Delta E$ stands for the total energy ($cm^{-1}$) relative to that of the most stable form (2A). The total energy is corrected by the zero-point vibrational energy. Numbers in parentheses represent the charge on each of the constituent $CS_2$ molecules.

the calculated frequencies of CS stretching vibrations of $CS_2$ and $CS_2^+$. For $CS_2^+$, the antisymmetric CS stretching band is predicted to appear at 1227 $cm^{-1}$, which does not agree with the IRPD results in Fig. 3(a). Therefore, the calculation also suggests the absence of the $CS_2^+$ ion core. The optimized structures of $C_2S_4^+$ are shown in Fig. 5. For $C_2S_4^+$, there are four optimized structures with the $C_2$, $C_{2h}$, $C_{2v}$, and $D_{2h}$ symmetry. The structures other than the $D_{2h}$ one have already been theoretically found by Zhou and Andrews.[30] In the optimized structures of $C_2S_4^+$, the positive charge is equally occupied by the two constituent molecules, even for the $C_{2v}$ form (2C). We cannot find any isomer that has a monomer cation core $CS_2^+$ in our calculations of $(CS_2)_2^+$. Isomer 2A [Fig. 5(a)] is the most stable form among the four isomers and is located at the potential minimum. Isomers other than 2A have imaginary vibrational frequencies. Geometry optimization with symmetry restriction to $C_{2h}$ provides isomer 2B. The normal mode with the imaginary frequency for 2B is recognized as an intermolecular out-of-plane bending motion, connecting isomer 2B with 2A. The energy difference between 2A and 2B is only 80 $cm^{-1}$. In addition, the lowest-frequency mode of 2A ($\sim$13 $cm^{-1}$) is also an intermolecular bending motion. Therefore, the $C_2S_4^+$ cation has a quite shallow potential along the out-of-plane bending motion. Isomers 2C ($C_{2v}$) and 2D ($D_{2h}$) are also saddle-point structures and have total energies much higher than those of 2A and 2B. Therefore, it is reasonable to rule out isomers 2C and 2D from the candidate of the $C_2S_4^+$ cation core in $(CS_2)_n^+$. The calculated frequencies of CS stretching vibrations of isomers

2A and 2B are also tabulated in Table I. The vibrations of 2A and 2B in the 1420–1440 $cm^{-1}$ region are interpreted as linear combinations of the antisymmetric CS stretching vibration of constituent $CS_2$ molecules. The out-of-phase combination mode of the two antisymmetric CS stretching vibrations [$b$ (2A) or $b_u$ (2B)] has an IR intensity stronger than that of the in-phase combination [$a$ (2A) or $a_g$ (2B)]. For isomer 2A, both of the CS stretching vibrations at 1432 and 1425 $cm^{-1}$ have nonzero IR intensity (401.66 and 136.79 km/mol, respectively). On the contrary, isomer 2B has only one IR-active mode at 1429 $cm^{-1}$ (519.65 km/mol). The appearance of the two bands around 1400 $cm^{-1}$ for 2A is consistent with the IRPD results that there are two IR bands assignable to $C_2S_4^+$ at around 1410

TABLE I. Vibrational frequency ($cm^{-1}$) and IR intensity (in parentheses, km/mol) of CS stretching vibrations for $CS_2$, $CS_2^+$, $CS_2^-$, and $C_2S_4^+$ calculated at the B3LYP/6-311+G* level of theory. A scaling factor of 0.9880 is employed for all the frequencies calculated.

| $CS_2$ | $CS_2^+$ | $CS_2^-$ | $C_2S_4^+$ (2A, ($C_2$)) | $C_2S_4^+$ (2B, ($C_{2h}$)) |
|---|---|---|---|---|
| 1535 (690.05) | 1227 (63.77) | 1149 (624.27) | 1432 (401.66, $b$)[a] | 1429 (519.65, $b_u$)[a] |
| 666 (0) | 658 (0) | 643 (18.02) | 1425 (136.79, $a$)[a] | 1426 (0, $a_g$)[a] |
| | | | 657 (1.67) | 659 (0) |
| | | | 656 (0.63) | 658 (3.03) |

[a]Alphabetical letters in parentheses represent irreducible representations of the normal modes in the $C_2$ (2A) or $C_{2h}$ (2B) symmetry.

and 1490 cm$^{-1}$. For isomer 2A, the IR intensity of the 1425 cm$^{-1}$ mode relative to that of the 1432 cm$^{-1}$ one is 136.79/401.66=0.34. This value agrees very well with the relative intensity ($\sim$0.38) observed for the 1410 and 1490 cm$^{-1}$ bands in the IRPD spectrum of $(CS_2)_3^+$. On the contrary, isomer 2B is not a stable structure. There is only one IR-active mode around 1400 cm$^{-1}$, which does not fit the IRPD spectral feature. Consequently, it is quite probable that the positive charge in $(CS_2)_n^+$ is localized in the dimer unit $C_2S_4^+$, which has a $C_2$ structure like isomer 2A.

Here, it is worth discussing the discrepancy between the results of IRPD spectroscopy and the matrix isolation experiments. Zhou and Andrews found only one IR band of $C_2S_4^+$ at $\sim$1380 cm$^{-1}$ in solid Ne and Ar.[30] They also carried out DFT calculations of $C_2S_4^+$ and obtained results similar to those in this study. It was concluded that the $C_2S_4^+$ ion in solid matrices has a slightly out-of-plane structure close to the $C_{2h}$ structure than the $C_2$ one. On the contrary, the IRPD results strongly suggest that the $C_2S_4^+$ cation existing in the $(CS_2)_n^+$ clusters has a $C_2$ form like isomer 2A. The difference in the structure of $C_2S_4^+$ between in solid matrices and in the gas phase may probably come from solvent effect of rare gas matrices. DFT calculations of $C_2S_4^+$ are done in the gas phase condition. Therefore, it is reasonable that the IRPD results coincide with those calculated, although the $C_2S_4^+$ cation is surrounded by solvent $CS_2$ molecules in the gas phase experiments. On the contrary, the $C_2S_4^+$ cation in solid matrices is completely surrounded by rare gas atoms and takes weak solvent effect from the atoms. As mentioned above, the potential energy surface along the out-of-plane motion, which connects isomer 2A with 2B, is quite shallow. Therefore, the solvent effect from matrices can easily change the $C_2S_4^+$ cation from a bent ($C_2$) to a planar ($C_{2h}$) structure even in rare gas matrices.

## B. $(CS_2)_n^-$

Figure 2(b) shows the mass spectrum of $(CS_2)_n^-$. Different from the case of cation clusters [Fig. 2(a)], the strongest signal corresponds to the $CS_2^-$ monomer anion. The ion intensity of $(CS_2)_n^-$ decreases monotonously with increasing the cluster size. Figure 3(b) shows the IRPD spectra of $(CS_2)_n^-$ for $n=3-10$ in the 1100–2000 cm$^{-1}$ region. Two peaks appear at $\sim$1215 and $\sim$1530 cm$^{-1}$. The 1530 cm$^{-1}$ band increases its relative intensity to the 1215 cm$^{-1}$ band with increasing the cluster size. Similar to the $(CS_2)_n^+$ cation clusters, the band at 1530 cm$^{-1}$ is assigned to the antisymmetric CS stretching vibration of solvent $CS_2$ molecules. The 1215 cm$^{-1}$ band is assignable to a CS stretching vibration of an anion core existing in $(CS_2)_n^-$. Since the position of the anion core band is almost the same for all the IRPD spectra in Fig. 3(b), all of the $(CS_2)_n^-$ clusters have a common anion core structure. Even the $(CS_2)_3^-$ cluster exhibits the solvent band, suggesting that the common anion core in the $(CS_2)_n^-$ clusters should be a monomer, $CS_2^-$, or dimer, $C_2S_4^-$.

In order to ascribe the anion core band of $(CS_2)_n^-$, we carried out geometry optimization and vibrational analysis of anion species. As shown in Fig. 4(c), geometry optimization of the $CS_2^-$ monomer anion provides a $C_{2v}$ structure. The antisymmetric CS stretching vibration of $CS_2^-$ is calculated

to appear at 1149 cm$^{-1}$ (see Table I). This frequency is comparable to the position of the IRPD band at $\sim$1215 cm$^{-1}$. Therefore, the anion core band at $\sim$1215 cm$^{-1}$ can be assigned to the monomer anion core $CS_2^-$ with a $C_{2v}$ form. The assignment of the 1215 cm$^{-1}$ band is supported by the results of IR spectroscopy in solid Ne and Ar; the antisymmetric CS stretching vibration of $CS_2^-$ was experimentally found at 1159.2 cm$^{-1}$ in solid Ne or 1160.4 cm$^{-1}$ in solid Ar, which is close to the position of the 1215 cm$^{-1}$ band in the IRPD spectra.[30] Here, we have to consider the possibility of the dimer anion core structure in $(CS_2)_n^-$ ($n=3-10$). Tsukuda $et$ $al.$ suggested in their PE paper of $(CS_2)_n^-$ that there is a small amount of electronic isomers with the $C_2S_4^-$ core for $n=3-6$.[32] Yu $et$ $al.$ reported IR spectra of $C_2S_4^-$ in solid Ne and Ar, and calculated vibrational frequencies for several structures of $C_2S_4^-$.[31] In their IR spectra, a peak arising from $C_2S_4^-$ appears at 909 cm$^{-1}$ in solid Ne. On the basis of the isotope effect of the IR spectra and their $ab$ $initio$ calculations, the $C_2S_4^-$ isomer that provides the 909 cm$^{-1}$ band has a planar C–C chemically bonded $D_{2h}$ structure. They also obtained four other $C_2S_4^-$ isomers in their calculations. Among the five $C_2S_4^-$ isomers, four structures delocalize the negative charge over the two constituent $CS_2$ molecules. Vibrational analysis of these charge-delocalizing isomers exhibits strong IR bands only below 1100 cm$^{-1}$. These previous results on $C_2S_4^-$ are consistent with the assignment of the 1215 cm$^{-1}$ band in the IRPD spectra to the $CS_2^-$ anion core. On the other hand, we cannot completely rule out the possibility of the existence of the $C_2S_4^-$ anion core in our experiment in the present stage. It is our future work to examine the dimer anion core species for $(CS_2)_n^-$ by measuring the IRPD spectra below 1100 cm$^{-1}$.

## IV. CONCLUSION

The ion core structure has been investigated for $(CS_2)_n^+$ and $(CS_2)_n^-$ with $n=3-10$ by infrared photodissociation (IRPD) spectroscopy in the 1100–2000 cm$^{-1}$ region. The IRPD spectra have been analyzed with the aid of quantum chemical calculations at the B3LYP/6-311+G* level of theory. The $(CS_2)_n^+$ clusters display two CS stretching bands assignable to the cation core at $\sim$1410 and $\sim$1490 cm$^{-1}$. The cation clusters of $(CS_2)_n^+$ have a symmetrical dimer cation core $C_2S_4^+$ that has a $C_2$ form; the charge resonance (CR) interaction occurs between two $CS_2$ molecules of $C_2S_4^+$ and forms a semicovalent bond between the sulfur atoms. In the case of $(CS_2)_n^-$, the IRPD spectra show a weak band at $\sim$1215 cm$^{-1}$. This band is ascribed to the antisymmetric CS stretching vibration of the $CS_2^-$ anion core with the $C_{2v}$ symmetry. In conclusion, the $(CS_2)_n^+$ and $(CS_2)_n^-$ clusters with $n=3-10$ have the $C_2S_4^+$ ($C_2$) and $CS_2^-$ ($C_{2v}$) ion cores, respectively.

## ACKNOWLEDGMENTS

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