Effects of isomer coexistence and solvent-induced core switching in the photodissociation of bare and solvated (CS$_2$)$_2^-$ anions

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The photodissociation of the (CS$_2$)$_2^-$ dimer anion, known to exist in the form of several electronic and structural isomers, has been investigated at 532, 355, and 266 nm. The observed anionic fragments are CS$_2^-$ and C$_2$S$_2^-$ at 532 nm, and C$_2$S$_3^-$, CS$_2^-$, S$_2^-$, and S$^-$ at 355 and 266 nm. In addition to the photon energy, the fractional yields of the photofragments depend on the ion source conditions and solvation of the dimer anion. Specifically, the (CS$_2^-$+$S^-$)/CS$_2^-$ product ratio is significantly higher when (CS$_2$)$_2^-$ is formed in the presence of water in the precursor gas mixture, even though the parent anion itself does not include H$_2$O. On the other hand, an abrupt decrease in the above product ratio is observed upon the addition of solvent molecules (CS$_2$ or H$_2$O) to the (CS$_2$)$_2^-$ anion. Since the variation of this product ratio exhibits positive correlation with the relative intensity of the photoelectron band assigned to the C$_2$S$_4^-$ (2B$_1$) covalent structure of C$_2$S$_4^-$ by Habteyes et al. [J. Phys. Chem. A 112, 10134 (2008)], this structure is suggested as the primary origin of the C$_2$S$_3^-$ and S$_2^-$ photoproducts. The switching of the fragmentation yield from C$_2$S$_2^-$ and S$_2^-$ to other products upon solvation is ascribed to the diminished presence of the C$_2$S$_4^-$ (2B$_1$) dimer-anion structure relative to the CS$_2^-$ based clusters. This population shift is attributed to the more effective solvation of the latter. The CS$_2^-$ based clusters are suggested as the origin of the S$^-$ photoproduct, while CS$_3^-$ is formed through the secondary S$^-$+CS$_2$ intracluster association reaction. © 2009 American Institute of Physics. [DOI: 10.1063/1.3094318]

I. INTRODUCTION

Carbon disulfide is used as a solvent and a building block in the synthesis of many organic compounds. The reactivity of CS$_2$ can be contrasted with that of isovalent CO$_2$ by referring to the thermochemical data on ion-molecule association and clustering reactions.$^1$ Carbon dioxide forms weakly bound complexes with positive ions due to the poor Lewis basicity of oxygen atoms, but it forms covalent bonds with negative ions (such as O$^-$) through nucleophilic attack on the carbon atom.$^2,3$ The CS$_2$ molecule, on the other hand, exhibits amphoteric character, forming covalent bonds with both positive and negative ions through its sulfur and carbon atoms, respectively.$^3$ In the gas-phase clustering reactions of CS$_2$ in a pulsed electron-beam high-pressure mass spectrometer, S$_2^-$, S$_2^-$·CS$_2$, and CS$_3^-$ ions were observed as minor products, in addition to the (CS$_2$)$_n^-$ clusters.$^4$ In the drift-tube study of the $^{34}$S$^-$+CS$_2$ reaction, the isotope-exchange (S$^-+^{34}$SCS) and sulfur abstraction ($^{34}$SS$^-$+CS) products were observed.$^5$ Although CS$_3^-$ was not detected directly, the formation of the long-lived CS$_3^-$ complex was suggested in the isotope-exchange process. However, in the S$_2^-$ channel, which was observed at collision energies above 0.3 eV, the $^{32}$S$^{32}$S$^-$ product was not observed, ruling out the formation of an intermediate CS$_{2n}^-$ collision complex.$^5$

Maeyama et al.$^6$ studied the photodissociation of (CS$_2$)$_n^-$, $n$=1–4, in the ∼1.0–2.8 eV photon energy range. Two dissociation channels, CS$_2^-$+CS$_2$ and C$_2$S$_3^-$+S$_2^-$, were observed for $n$≥2. Although the channel branching ratios could not be quantified, it was suggested that the same cluster core was involved for all $n$ in the $n$=2–4 range, as the total photodepletion cross section peaked between 1.6 and 1.8 eV for all the clusters studied. These results were interpreted$^6$ considering the C$_2$S$_4^-$ structure of C$_2$O symmetry (corresponding to the $^2B_1$ electronic state), in which the two CS$_2$ moieties are bound by the covalent C−C and S−S bonds. This dimer-anion structure (shown in Fig. 1) had been predicted earlier$^4$ based on theoretical calculations. The photoelectron spectra measured by Tsukuda et al.$^7$ confirmed the existence of the covalent dimer-anion. The bands corresponding to the CS$_2^-$ and C$_2$S$_3^-$ based clusters were observed for (CS$_2$)$_n^-$ with $n$ up to 6. In the intracluster reactions of (CS$_2$)$_n^-$ induced by surface impact at a collision energy of 50 eV, Kondow and co-workers$^8$ observed the S$^-$, C$_2$S$^-$, S$_2^-$, CS$_2^-$, and C$_2$S$_2^-$ fragments for $n$=2, and S$^-$, S$_2^-$, and CS$_2^-$ for $n$=3.

In addition to the above C$_{2n}^-$ (2B$_1$) structure,$^{6,9}$ other isomers have been proposed for (CS$_2$)$_2^-$, which include several distinct covalently bound structures.$^{7,10–13}$ Recently, we reported a photoelectron imaging study of (CS$_2$)$_2^-$ under varying ion-source and solvation conditions.$^{14}$ With the aid of theoretical calculations,$^{15}$ the bands in the photoelectron images and spectra were assigned to the CS$_2^-$, CS$_2$·CS$_2$, and two covalent structures, C$_{2n}^-$ (2B$_1$) and D$_{2h}^-$ (2B$_3$), shown in Fig. 1. The C$_{2n}^-$ (2B$_1$) isomer was con-

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the precursor delivery line, corresponding to the so-called “wet source conditions.” Under the dry conditions, the \((\text{CS}_2)_n^-\) cluster progression is most abundant in the parent-ion mass spectra. With the “wet” source, the \((\text{CS}_2)_n^-(\text{H}_2\text{O})_m\) cluster anions are most prominent (see Fig. 2 in Ref. 14).

The negative ions are pulse extracted from the source chamber into the 2.3 m long flight tube of a Wiley–McLaren time-of-flight mass spectrometer. The ions are accelerated to a kinetic energy of about 3 keV and brought to a temporal and spatial focus in the detection region of the instrument with a base pressure of \(5 \times 10^{-9}\) Torr, where they are detected with an in-line microchannel plate (MCP) detector mounted at the end of the flight tube.

A pulsed laser beam is timed to overlap with the mass-selected cluster anions of interest and the resulting photofragments are mass analyzed using a reflectron time-of-flight mass spectrometer and a second off-axis MCP detector. The experiments are performed with the 532, 355, and 266 nm harmonics of a neodymium-doped aluminum garnet laser (Spectra Physics Laboratory 130, 50 Hz pulse repetition rate), with approximate pulse energies of 30, 15, and 5 mJ, respectively. The photofragment mass spectra are recorded by accumulating the pre-amplified ion signals from the off-axis MCP detector over 512 experimental cycles using a digital oscilloscope.

### III. RESULTS

In Sec. III A, we describe the photofragmentation pathways of hydrated \(\text{CS}_2^-\) ions. These results set the stage for the discussion of the contrasting fragmentation patterns of cluster anions containing the \(\text{CS}_2^-\) and \(\text{C}_2\text{S}_4^-\) ionic cores (Sec. III B). In Sec. III C, the effect of the formation conditions on the fragmentation pathways of (nominally) the same cluster anions is considered.

#### A. Photodissociation of bare and hydrated \(\text{CS}_2^-\)

The photofragment-ion mass spectra for the \(\text{CS}_2^-(\text{H}_2\text{O})_m\) parent anions collected at 355 and 266 nm are presented in Figs. 2(a) and 2(b), respectively. The spectra are normalized to the same maximum intensity not representative of the absolute dissociation cross sections. At 355 nm, the \(\text{S}^-\) based products appear for \(m=0–5\). As \(m\) increases, the \(\text{CS}_2^-\) fragment is first seen for \(m=2\) and its hydrates become the only observed product type for \(m=6–8\). At 266 nm, no anionic photofragments are observed for \(m=0\) and 1, indicating that a minimum of two water molecules is required to enable the photodissociation, as opposed to the photodetachment of \(\text{CS}_2^-\) at this wavelength. The 266 nm fragments observed for \(m \geq 2\) are similar to the 355 nm results, with a slight variation in the relative peak intensities.

#### B. Photofragmentation of \((\text{CS}_2)_n^-\) and \((\text{CS}_2)_2^-(\text{H}_2\text{O})_m\) cluster anions

The photofragment mass spectra for the \((\text{CS}_2)_n^-\), \(n = 2–4\), and \((\text{CS}_2)_2^-(\text{H}_2\text{O})_m\), \(m=0–2\) parent anions obtained at 532, 355, and 266 nm are presented in Figs. 3(a) and 3(b), respectively. While the fragment distributions depend, as expected, on photon energy and the number of solvating \(\text{CS}_2\) or

![Diagram](image-url)
H$_2$O molecules, they also exhibit a less intuitive, yet significant, dependence on the ion source conditions, specifically the presence of water in the precursor gas mixture. The spectra in Fig. 3(a) were obtained under the dry source conditions, while those in Fig. 3(b) correspond to the wet source conditions. The moisture effect on the fragmentation of (nominally) the same parent anion, (CS$_2$)$_2^-$, can be seen by comparing the $n=2$ spectra in Fig. 3(a) to the corresponding $m=0$ spectra in Fig. 3(b). Of the several photofragment types, we particularly emphasize the relative yields of CS$_2^-$, on the one hand, and C$_2$S$_2^-$ and S$_2^-$, on the other. The (C$_2$S$_2^- + S_2^-$/CS$_2^-$) product ratios determined for the different wavelengths and parent ions are summarized in histogram form in Fig. 4.

As also seen in Fig. 3, the simplest fragmentation patterns are observed at 532 nm. At this wavelength, (CS$_2$)$_2^-$ dissociation yields the CS$_2^-$ and C$_2$S$_2^-$ fragment ions with comparable intensities regardless of the source conditions. However, upon solvation with additional CS$_2$ or H$_2$O molecules, the C$_2$S$_2^-$ channel is effectively turned off, as reflected in the 532 nm spectra in Fig. 3(a) for $n=3–4$ and Fig. 3(b) for $m=1–2$.

At 355 nm, the S$_2^-$ and CS$_3^-$ anionic fragments are also observed for (CS$_2$)$_n^-$, in addition to the CS$_n^-$ and C$_2$S$_2^-$ products. The C$_2$S$_2^-$ ion is the most intense 355 nm photofragment for the (CS$_2$)$_2^-$ parent anion. However, with the addition of just one more CS$_2$ solvent molecule, the C$_2$S$_2^-$ and S$_2^-$ product channels decrease significantly. Similar to the 532 nm result, in larger clusters the CS$_2^-$ fragment takes a central stage, as seen in Fig. 3(a) for $n=3–4$.

At 266 nm, the C$_2$S$_2^-$ channel remains dominant for fragmentation of (CS$_2$)$_2^-$ under both the dry and wet source conditions, while the CS$_2^-$ yield diminishes further compared to the 355 and 532 nm results. This trend is accompanied by a relative increase in S$_2^-$ and the appearance of the S$^-$ product. Again, the addition of the CS$_2$ solvent turns off, nearly completely, the S$_2^-$ and C$_2$S$_2^-$ product channels, along with S$^-$, while enhancing the relative intensities of CS$_2^-$ and CS$_3^-$.

C. The effect of water in the ion source

As seen in Figs. 3(a) and 3(b), CS$_2^-$ is the only 352 nm anionic product for both the (CS$_2$)$_n^-$, $n=3–4$, and (CS$_2$)$_2^-(H_2O)_m$, $m=1–2$ cluster anions, with the exception...
of a minor CS$_2^-$·H$_2$O signal observed for (CS$_2$)$_2$·(H$_2$O)$_m$. At 355 and 266 nm, however, the fragmentation patterns of the hydrated clusters are drastically different from those of (CS$_2$)$_2^-$. Even the unhydrated (CS$_2$)$_2^-$/parent anion exhibits different channel branching ratios depending on the ion source conditions. The C$_2$S$_2^-$/product fraction is larger for the “wet” source, as seen by comparing the 355 and 266 nm results for $m=0$ in Fig. 3(b) to those for $n=2$ in Fig. 3(a). This trend persists in the (CS$_2$)$_2^-$/H$_2$O$_m$, $m=1–2$, clusters. As seen in Fig. 4, the C$_2$S$_2^-$(H$_2$O)$_m$/C$_2$S$_2$- product ratio is always larger within the hydrated cluster series (generated under the wet source conditions) compared to the (CS$_2$)$_n$- series (formed in a dry source).

The large error bars for the (CS$_2$)$_2^-$/H$_2$O$_m$ parent-ion series in Fig. 4 reflect the variation in the photofragment yields between different experimental runs. These variations result from the day-to-day fluctuations in the concentration of H$_2$O in the gas delivery lines. No variations in such significant magnitude were observed in the fragmentation patterns when the ion source was kept consistently moisture-free. This observation itself indicates that not just the relative intensities, but also the structural and, therefore, photochemical properties of the (CS$_2$)$_2^-$ and (CS$_2$)$_2^-$/H$_2$O$_m$, $m=1–2$, cluster ions are affected by the presence of H$_2$O at the ion formation stage.

The fractional yield of C$_2$S$_2^-$ from (CS$_2$)$_2^-$ is positively correlated with the intensity of the C$_2$S$_2$ (2$^B_1$) band in the corresponding photoelectron spectrum. Both the C$_2$S$_2$- fragment fraction (at 355 and 266 nm) and the intensity of the photoelectron band increase under the wet source conditions. Hence, we conclude that the presence of H$_2$O in the ion source enhances the formation of the C$_2$S$_2$ (2$^B_1$) isomer of C$_2$S$_4^-$ that in turn gives rise to the C$_2$S$_2^-$ photofragments.

Summarizing the results, (i) the fractional yield of C$_2$S$_2^-$ and S$_2^-$ from the bare (CS$_2$)$_2^-$, and S$_2^-$ from the presence of H$_2$O at the ion formation stage and (ii) solvation by additional CS$_2$ or H$_2$O decreases the fractional yield of the C$_2$S$_2^-$ and S$_2^-$ fragments, mainly in favor of the CS$_2^-$ channel. Comparing Figs. 3(a) and 3(b), particularly the 355 nm data, it may appear that H$_2$O is less effective in turning off the C$_2$S$_2^-$ and S$_2^-$ channels compared to the CS$_2^-$ solvent. However, this is largely due to the more abundant presence of the C$_2$v (2$^B_1$) isomer under the wet source conditions.

IV. DISCUSSION

A. The dissociation channels of CS$_2^-$·(H$_2$O)$_m$

Similar to the photodissociation of hydrated CO$_2^-$ in water clusters, two types of dissociation channels are observed for CS$_2^-$·(H$_2$O)$_m$ at 355 and 266 nm: (i) the core-dissociation channel, where the CS$_2^-$ cluster core dissociates into S$^-$/CS accompanied by loss of several water molecules, and (ii) the solvent-evaporation channel, where the photon energy is dissipated by the evaporation of several solvent molecules, while the CS$_2^-$ anion remains intact.

B. The dissociation channels of (CS$_2$)$_2^-$

In the first photofragmentation experiment on (CS$_2$)$_2^-$ at photon energies of up to ~2.8 eV, Maeyama et al. observed only the CS$_2^-$ and C$_2$S$_3^-$ fragmentation products. The present findings at 532 nm (2.33 eV) are in line with this result. However, our experiments at 355 and 266 nm reveal additional processes that were not observed previously. First, the C$_2$S$_2^-$ product channel becomes dominant as the photon energy increases. Second, in addition to CS$_2^-$ and C$_2$S$_3^-$, we observed new S$^-$, S$_2^-$, and CS$^-$/products.

These photofragments are plausibly associated with the following pathways:

$$C_2S_4^-(or \; CS_2^- \cdot CS_2) + h\nu \rightarrow CS_2^- + CS_2,$$

(1)

$$C_2S_4^- + h\nu \rightarrow C_2S_2^- + S_2,$$

(2)

$$C_2S_4^- + h\nu \rightarrow S_2^- + C_2S_2,$$

(3)

$$CS_2^- \cdot CS_2 + h\nu \rightarrow S^- + CS + CS_2,$$

(4)

$$C_2S_2^- \cdot CS_2 + h\nu \rightarrow CS + S^- \cdot CS_2 \rightarrow CS + CS_3^-.$$

(5)

These dissociation channels are summarized in Fig. 5, which shows the proposed reactant structures, intermediates, and products correlations for (CS$_2$)$_2^-$. Similar pathways, involving additional solvent molecules, are expected for the larger (CS$_2$)$_n^-$ and (CS$_2$)$_2^-$/H$_2$O$_m$ clusters.

The parent structures included in Fig. 5 are selected based on the photoelectron imaging results. The relative parent and product-channel energies are from the CCSD(T)/6-311+G(3df) calculations. The C$_2$v (2$^B_1$) structure is predicted to be the most stable (CS$_2$)$_2^-$ structure. This structure and the next higher-lying one, $D_{2h}$ (2$^B_3$), are characterized by a “doubly excited” electron configuration of the neutral core. That is, the removal of the
form the CS$_2^-$ photoproduction by predissociation of the CS$_2^-$·CS$_2$ complex or by caging of the S$^+$·CS photofragments of its anionic core. Hence, channel (1) can, in principle, involve any of the proposed (CS$_2$)$_2^-$ isomers. Channels (2) and (3), on the other hand, are most consistent with the lowest-energy C$_{2v}$ ($^2B_1$) structure, which contains a pre-existing S–S bond.

The straightforward mechanism accounting for the S$^-$ fragments is the dissociation of CS$_2^-$ based clusters [channel (4)], analogous to CO$_2^-$→CO+O$^-$ dissociation$^{16,18}$ Channel (5), yielding the CS$_3^-$ photofragments, is also possible in CS$_2^-$ based clusters, assuming that the core dissociation is followed by an ion-molecule association reaction with solvent CS$_2$. This two-step process is analogous to the CO$_3^-$ channel in (CO$_2$)$_m^-$ and (CO$_2$)$_2^-$(H$_2$O)$_m$.

C. Fragment origins and mechanisms

The S$^-$ and CS$_3^-$ products. In the photodissociation of CS$_2^-$·(H$_2$O)$_m$, the S$^-$ product is observed for $m=0$–5 at 355 nm [Fig. 2(a)] and for $m=2$–5 at 266 nm [Fig. 2(b)]. For (CS$_2$)$_2^-$ prepared under the dry source conditions, the S$^-$ product is essentially absent at 355 nm, while CS$_3^-$ is observed [Fig. 3(a)]. The formation of S$^-$ from solvated CS$_2^-$ is possible when, first, the photon energy is large enough to overcome the dissociation threshold and, second, there is sufficient solvent-induced stabilization of excited CS$_2^-$ states (CS$_2^-$) enabling the CS$_2^-$→CS+S$^-$ dissociation to compete successfully with CS$_2^-$ autodetachment.

By comparing the 266 nm spectra in Fig. 3(a) for $n=2$ and Fig. 3(b) for $m=0$, both of which correspond to (nominally) the same (CS$_2$)$_2^-$ parent anions, a larger S$^-$ fragment fraction is observed under the dry source conditions. In light of the proposed channel (4) mechanism, this observation parallels the conclusion drawn from the previous photoelectron imaging study, namely, the presence of water in the ion source enhances the formation of the more stable covalent C$_2$S$_4^-$ dimers over CS$_2^-$·CS$_2$, of which the latter is primarily responsible for the S$^-$ photofragments. The disappearance of S$^-$ in the (CS$_2$)$_2^-$, $n=3$–4 fragment mass spectra in Fig. 3(a) reflects, in part, the competition with channel (5), involving a secondary reaction of nascent S$^-$ with the CS$_2$ solvent.

Based on the mechanism suggested for channel (5), the CS$_2^-$ product intensity should reflect the populations of the CS$_2^-$ based parent clusters, CS$_2^-$·(CS$_2$)$_{n-1}$, or CS$_2$·CS$_2$·(H$_2$O)$_m$. Indeed, in Figs. 3(a) and 3(b), the intensity of CS$_2^-$ relative to other photofragments is consistently higher under dry source conditions, compared to the results in a “wet” ion source. Again, this indicates a positive correlation between a process involving a monomeric CS$_2^-$ cluster core and the absence of water in the ion source (even when the parent anions themselves do not contain H$_2$O).

The largest relative yield of CS$_2^-$ is observed at 266 nm for (CS$_2$)$_2^-$, $n=3$ and 4, where it is in fact the dominant product. On the other hand, no CS$_3^-$ is observed at the same wavelength from any of the (CS$_2$)$_2$·(H$_2$O)$_m$ clusters studied, despite the presence of S$^+$ fragments and the availability of a solvent CS$_2$ molecule for a secondary S$^+$·CS$_2$→CS$_3^-$ reaction. This may be a consequence of the structural differences.
between the two types of clusters. In $\text{CS}_2^-\,(\text{H}_2\text{O})_m$, more $\text{CS}_2$ molecules become available with increasing $n$ for the secondary $\text{S}^++\text{CS}_2$ association step in Eq. (5), resulting in the observed increase in the $\text{CS}_2^-$ fragment intensity from $n = 2$ to $n = 3-4$. In $\text{CS}_2$, $\text{CS}_2^-\,(\text{H}_2\text{O})_m$, on the other hand, the water molecules occupying the most favorable solvation sites near $\text{CS}_2^-$ will hinder the secondary reaction.

Although $\text{CS}_3^-$ is stable by $\sim 1.7$ eV with respect to $\text{S}^++\text{CS}_2$, it was not observed in the drift-tube experiment by Lee and Bierbaum. The authors suggested that due to the large polarizability of $\text{CS}_2$ and relatively low center-of-mass energy, long-lived $\text{CS}_3^-$ collision complex could be formed through nucleophilic attack on the carbon. In their experiment, the isotope exchange reaction was observed at collision energies below 0.3 eV, while both the isotope exchange and sulfur abstraction took place above 0.3 eV. The absence of the $\text{CS}_3^-$ products above 0.3 eV indicates that the sulfur abstraction occurs through direct attack on the sulfur atom, ruling out the formation of $\text{CS}_3^−$. The observation of $\text{CS}_3^-$ in our experiment signals a greater efficiency of the association reaction within a cluster environment, compared to the drift tube experiment.

**The $\text{CS}_2^-$ product.** In the photofragmentation of the $\text{CS}_2^-(\text{H}_2\text{O})_m$ clusters, $\text{CS}_2^-$ fragments are observed for $m \geq 2$ at 355 nm and for $m \geq 3$ at 266 nm (see Fig. 2). The photoinduced excitation of the cluster core should lead to $\text{CS}_2^-\rightarrow\text{CS}+\text{S}^-$ dissociation and/or $\text{CS}_2^+$ autodetachment. Since water does not absorb at these wavelengths, the plausible mechanism for $\text{CS}_2^-$ fragment formation is via the solvent-induced relaxation of $\text{CS}_2^+$ or fragment caging.

The fractional yields of $\text{CS}_2^-$ from $(\text{CS}_2)_2^-$ and $(\text{CS}_2)_2^-(\text{H}_2\text{O})_m$ (see Fig. 3) are generally much larger than those from $(\text{CS}_2)_2^-(\text{H}_2\text{O})_m$. This is to be expected, as the dimer based cluster anions are more likely to yield $\text{CS}_2^-$ via $\text{C}_2\text{S}_4^-\rightarrow\text{CS}_2^-+\text{CS}_2$ dissociation. As seen in Fig. 3, upon addition of $\text{CS}_2$ or $\text{H}_2\text{O}$ to $(\text{CS}_2)_2^-$, the relative yields of the $\text{C}_2\text{S}_4^-$ and $\text{CS}_2^-$ channels tend to decrease in favor of $\text{CS}_2^-$. This channel switching is in positive correlation with the solvent molecules serving as an effective heat sink, stabilizing the metastable structures, more abundant under the wet source conditions compared to that in the dry source.

**D. Channel switching versus $(\text{CS}_2)_2^-$ isomer coexistence**

The variation in the fragment intensities in $(\text{CS}_2)_2^-$ dissociation depending on the parent ion source conditions, as well as the observed dominant channel switching from $\text{C}_2\text{S}_2^-\,$ and $\text{S}^-\,$ to $\text{CS}_2^-\,$ upon salvation, are easily reconciled with the variations in the corresponding photoelectron spectra, reported separately. The dependence of the $(\text{CS}_2)_2^-$ fragmentation pattern on the presence of water in the precursor gas line is due to the role of $\text{H}_2\text{O}$ in facilitating the formation of the global minimum structure of the dimer anion, which dissociates mainly into $\text{C}_2\text{S}_2^-+\text{S}_2^-\,$ or $\text{S}_2^-+\text{C}_2\text{S}_2^-\,$. In addition to mediating the formation of the equilibrium structure, the water molecules serve as an effective heat sink, stabilizing the residual cluster anion by evaporation. As the photoelectron imaging results indicate, the $(\text{CS}_2)_2^-$ anions formed in the dry source are more likely to be trapped in the initially formed, yet less stable $\text{CS}_2^-\cdot\text{CS}_2$ structure, which is less likely to give rise to the $\text{C}_2\text{S}_2^-$ and $\text{S}_2^-$ products. The formation of the metastable structures, more abundant under the dry source conditions, is attributed to the anion stabilization processes after electron attachment, which mainly involves evaporation of the weakly bound $\text{CS}_2$ molecules or Ar atoms leading to an efficient trapping of the dimer anion in its initially accessible local minima.

When one or more solvent molecules (CS$_2$ or H$_2$O) are added to $(\text{CS}_2)_2^-$, the relative population of the dimer-core structure declines due to more favorable solvation of CS$_2^-$ versus C$_2$S$_4^-$. The observed decrease in the (C$_2$S$_2^-+S_2^-)/CS$_2^-$ product ratio reflects the diminishing presence of the global-minimum C$_{2v}$ (2$B_1$) core anions upon salvation.

**V. SUMMARY**

The photodissociation of $(\text{CS}_2)_2^-$ at 532, 355, and 266 nm has been investigated using tandem time-of-flight mass spectroscopy. Several fragmentation channels are observed, yielding the CS$_2^-$, C$_2$S$_2^-$, CS$_3^-$, S$_2^-$, and S$^-$ products. The channel branching ratios vary significantly, depending on the presence of water in the precursor gas mixture. Although $(\text{CS}_2)_2^-$ itself does not contain H$_2$O, the observed
variations in the fragmentation patterns reflect the effect of water presence at the ion formation stage on the resulting (CS$_2$)$_2^-$ isomer distribution. Specifically, the (C$_2$S$_2^-$ + S$_2^-$)/CS$_2^-$ channel ratio exhibits a striking positive correlation with the relative intensity of the photoelectron band attributed to the C$_2$ ($^2B_1$) covalent dimer-anion structure. This C$_2$S$_4^-$ structure is therefore identified as the primary origin of the C$_2$S$_2^-$ and S$_2^-$ photoproducts, while the CS$_2^-$···CS$_2$ ion-molecule complex is seen as the origin of S$^-$ and CS$_3^-$.

The fragmentation patterns also change drastically with the addition of solvent molecules (CS$_2$ or H$_2$O) to (CS$_2$)$_2^-$.

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