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Infrared Spectra of $(CS_2)_2^-$ Anion in Solid Neon and Argon

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Charged transient species produced from high-frequency discharge of CS_2 have been trapped in solid argon and neon. Besides the previously identified CS_2^-, CS_2^+, and $(CS_2)_2^+$ species, new absorptions at 909.0 cm^{-1} in solid neon and 908.0 cm^{-1} in solid argon were observed. Isotopic substitutions ($^{13}CS_2$, $C^{34}S_2$, and mixtures) showed that the new species involves two equivalent CS_2 subunits. The photosensitive behavior and the agreement with frequencies and isotopic frequency ratios from quantum chemical calculations substantiate assignment of these absorptions to the most stable isomer of the $(CS_2)_2^-$ anion, which was predicted to have a planar C−C chemically bonded D_{2h} structure.

Introduction

The formation, structures, and reactivities of carbon disulfide cluster anions have been investigated both experimentally and theoretically.[1−8] The $(CS_2)_2^-$ dimer anion is of particular interest as it is the core structure of large $(CS_2)_n^-$ clusters.[3] The gas-phase equilibria of the $CS_2^- + CS_2 \leftrightarrow (CS_2)_2^-$ reaction were studied by Hiraoka et al.[1] using a pulsed electron-beam high-pressure mass spectrometer. The $CS_2^-\cdots(CS_2)$ bond dissociation energy was determined to be 21.9 kcal/mol. Their calculations at the ROHF/6-31G level predicted two stable structures of $(CS_2)_2^-$, a $CS_2 \cdot CS_2^-$ complex having C_s symmetry and a C−C and S−S chemical-bonded anion with four-membered ring structure and C_{2v} symmetry. The C_{2v} structure was predicted to be 14 kcal/mol more stable than the C_s complex.[1] Tsukuda et al.[2] measured the photoelectron spectrum of $(CS_2)_2^-$ at a photon energy of 4.66 eV. They assigned the lowest energy peak at an electron binding energy of 1.65 eV to the C_s complex, and a peak at an electron energy of 2.7 eV to the C_{2v} form of the anion.[2] More recently, Maeyama et al.[3] reported the photodestruction spectra of $(CS_2)_n^-$, $n = 2−4$.[3] Their results indicated that $(CS_2)_2^-$ is the core structure of $(CS_2)_n^-$ cluster anions. The observation of the $C_2S_2^-$ product channel in the photodissociation of $(CS_2)_n^-$ clusters provided strong support for the cyclic C_{2v} form of $(CS_2)_2^-$. The electronic structure of $(CS_2)_2^-$ was theoretically investigated by Sanov et al.[7] at the MP2/6-31+G* level. Five different low-lying forms, including the ion−molecule complex and four covalent bounded anions, were identified. The most stable form was predicted to be covalently bonded and have a cyclic C_{2v} structure. The structure and vibrational frequencies of $(CS_2)_2^-$ were also studied by Zhang et al.[8] at the B3LYP/6-31+G* level. Five stable structures, including two ion−molecule complexes and three chemical compounds, were found. The most stable structure was predicted to have planar D_{2h} symmetry and an energy 16.58 kcal/mol lower than the sum of the energies of $CS_2 + CS_2^-$. It is noteworthy that the most stable structure of $(CS_2)_2^-$ is still not clear, and there are no infrared spectroscopic data for the $(CS_2)_2^-$ anion.

In previous pulsed-laser ablation experiments with metals and carbon dioxide and microwave discharge experiments, the CO_2^- and CO_2^+ charged species were produced and trapped in solid matrixes. The $(CO_2)_2^+$ and $(CO_2)_2^-$ cluster species were formed on annealing to allow association and reaction of carbon dioxide molecules.[9−11] In similar experiments with carbon disulfide, the CS_2^+, CS_2^-, and $(CS_2)_2^+$ species were also produced, but the $(CS_2)_2^-$ anion was not observed even on annealing, which suggests that the $(CS_2)_2^-$ anion cannot be formed via a $CS_2 + CS_2^-$ association reaction in solid matrix.[12] Previous gas-phase studies also suggest that there is energy barrier for the formation of $(CS_2)_2^-$ from the $CS_2 + CS_2^-$ reaction.[1]

In this paper, we report vibrational spectroscopic and quantum chemical calculations of the $(CS_2)_2^-$ anion produced by condensation of high-frequency discharged CS_2 in excess neon and argon.

Experimental and Computational Methods

The experimental setup for high-frequency discharge and matrix isolation FTIR spectroscopic investigation has been described in detail previously.[13,14] Briefly, the gas stream containing CS_2/Ar or CS_2/Ne was subjected to high-frequency discharge from a Tesla coil and was deposited onto a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. The matrix gas-deposition rate was typically 2−4 mmol per hour. In general, matrix samples were deposited for 0.5 to 2 h. The CS_2/rare gas mixtures were prepared in a stainless steel vacuum line using standard manometric technique. The CS_2 was cooled to 77 K using liquid N_2 and evacuated to remove volatile impurities. Isotopic labeled $^{13}CS_2$ and $C^{34}S_2$ (Isotec, 99%) were used without further purification. Infrared spectra were recorded on a Bruker Equinox 55 spectrometer at 0.5-cm^{-1} resolution using a DTGS detector. Matrix samples were annealed at different temperatures, and selected samples were subjected to broadband irradiation using a high-pressure mercury arc lamp and glass filters.

Quantum chemical theoretical calculations were performed using the Gaussian 98 program.[15] The Becke three-parameter

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hybrid functional with the Lee−Yang−Parr correlation corrections (B3LYP) was used.[16,17] Additional comparison ab initio calculations were also done using the second-order Moller−Plesset perturbation theory (MP2).[18] The 6-311+G* basis set was used for C and S atoms.[19,20] Geometries were fully optimized at both levels of theory, and vibrational frequencies were calculated at the B3LYP/6-311+G* level with analytical second derivatives, and zero point vibrational energies (ZPVE) were derived.

Results and Discussion

Microwave and high-frequency discharges have often been used in conjunction with the matrix isolation technique to produce and trap unstable species for spectroscopic studies. Numerous species, such as free radicals and charged ions that are difficult to study in the gas phase, have been produced and trapped in solid matrixes.[21] The products from condensation of a Tesla-coil-discharged CS_2/Ar have been investigated previously by Andrews et al.,[22] and absorptions due to CS, $(CS)_2$, C_2S_3, and C_3S_2 were observed. In the present study, an extensive series of experiments was performed with CS_2/Ar and CS_2/Ne samples under a variety of experimental conditions. The product absorptions depended strongly on the power levels of the discharge. Generally, the CS (1272.3 cm^{-1} in Ne, 1275.0, and 1270.0 cm^{-1} in Ar) and C_2S_3 (2078.2 and 1024.3 cm^{-1} in Ar)[22] absorptions dominated at a high power of discharge, while the charged species CS_2^+ (1206.8 cm^{-1} in Ne, 1200.5 cm^{-1} in Ar),[23] CS_2^- (1159.2 cm^{-1} in Ne, 1160.5 cm^{-1} in Ar),[12,24] and $(CS_2)_2^+$ (1385.2 cm^{-1} in Ne, 1379.7 cm^{-1} in Ar)[12] became obvious when relatively low power was employed. The relative intensities of the charged species also depended strongly on the CS_2 concentrations. In lower CS_2 concentration experiments, the CS_2^- and CS_2^+ absorptions were strong and the $(CS_2)_2^+$ absorption was weak. The $(CS_2)_2^+$ absorption increased on annealing at the expense of CS_2^+. Previous studies have shown that the $(CS_2)_2^-$ anion was not formed on annealing in solid matrixes with considerable CS_2^- and CS_2 present, suggesting that $(CS_2)_2^-$ cannot be formed by the $CS_2^- + CS_2$ association reaction without activation energy.[12] The $(CS_2)_2^-$ anion may also be formed through electron capture by the $(CS_2)_2$ van der Waals dimer. Therefore, we employed relatively high CS_2 concentrations. In higher CS_2 concentration experiments, the CS_2^+ and CS_2^- absorptions were very weak, but the $(CS_2)_2^+$ absorption was strong after sample deposition. Besides these known product absorptions, a new absorption was also observed. The spectra in the 920−880-cm^{-1} region with 0.8% CS_2 in Ne, which is of particularly interest here, is shown in Figure 1. The new 909.0-cm^{-1} absorption was observed on sample deposition, almost doubled on $\lambda > 400$ nm irradiation with a high-pressure mercury arc lamp (Figure 1, trace b). Continued irradiation with $\lambda > 290$ nm (Figure 1, trace c) reduced the 909.0-cm^{-1} absorption about 40%. Further broadband irradiation without pass filter reduced the band about 80% (Figure 1, trace d). The band intensity remained almost unchanged on subsequent annealing to 8 K (Figure 1, trace e).

Similar experiments were repeated with the $^{13}C^{32}S_2$, $^{12}C^{32}S_2 + {}^{13}C^{32}S_2$, $^{12}C^{34}S_2$, and $^{12}C^{32}S_2 + {}^{12}C^{34}S_2$ samples. The infrared spectra in the 920−870-cm^{-1} region using different isotopic samples are shown in Figure 2. The isotopic shifts and splittings of the product absorptions will be discussed below.

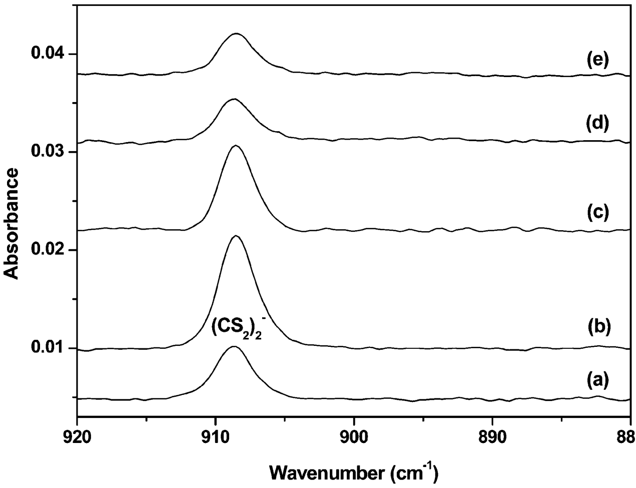

Figure 1. Infrared spectra in the 920−880-cm^{-1} region from condensation of high-frequency discharged 0.8% CS_2 in neon at 4 K. (a) After 1 h of sample deposition, (b) after 15 min of $\lambda > 400$ nm irradiation, (c) after 15 min of $\lambda > 290$ nm irradiation, (d) after 15 min of boardband irradiation, and (e) after 8-K annealing.

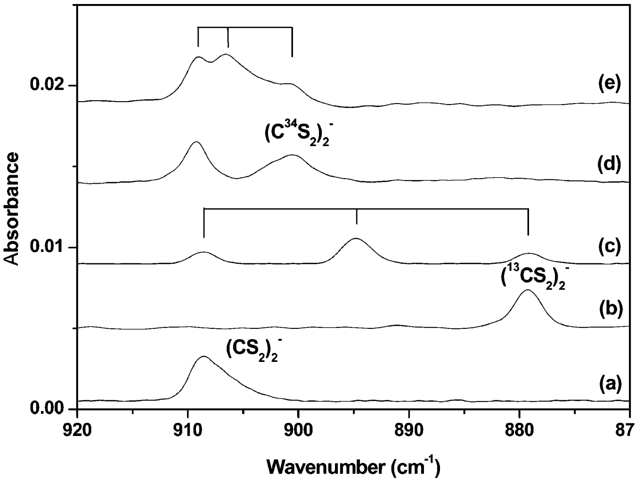

Figure 2. Infrared spectra in the 920−870-cm^{-1} region from condensation of high-frequency discharged CS_2/Ne mixture at 4 K followed by 15 min $\lambda > 400$ nm irradiation. (a) 0.8%$^{12}C^{32}S_2$, (b) 0.6%$^{13}C^{32}S_2$, (c) 0.3%$^{12}C^{32}S_2$ + 0.3%$^{13}C^{32}S_2$, (d) 0.6%$^{12}C^{34}S_2$, and (e) 0.3%$^{12}C^{32}S_2$ + 0.3%$^{12}C^{34}S_2$.

The same discharge experiments were done with the CS_2/Ar samples. The spectra in the 920−870-cm^{-1} region are shown in Figure 3. The counterpart of the 909.0-cm^{-1} band in solid neon was observed at 908.0 cm^{-1} in solid argon. This band was present on sample deposition (Figure 3, trace a), increased on $\lambda > 400$ nm irradiation (trace b), stayed almost unchanged on 25 K annealing (trace c), and was destroyed on $\lambda > 290$ nm irradiation (trace d).

The absorption at 909.0 cm^{-1} in solid neon shifted to 879.3 cm^{-1} in the $^{13}C^{32}S_2$ spectrum (Figure 2, trace b), and gave the $^{12}C/^{13}C$ isotopic frequency ratio of 1.0338. This band split into two bands at 909.2 and 900.4 cm^{-1} in the $^{12}C^{34}S_2$ spectrum (Figure 2, trace d). The 900.4-cm^{-1} band is the isotopic counterpart, which gave an isotopic $^{32}S/^{34}S$ ratio of 1.0096. The 909.2-cm^{-1} band is most likely a combination band of low-lying levels in Fermi resonance with the 900.4-cm^{-1} band. The isotopic frequency ratios are quite close to those of the antisymmetric CS_2 stretching mode of CS_2 (1.0337 and 1.0046) and CS_2^- (1.0330 and 1.0049) in solid neon, indicating that the 909.0-cm^{-1} band is due to an antisymmetric S−C−S stretching vibration. A triplet at 909.0, 894.9, and 879.3 cm^{-1} was observed in the mixed $^{12}C^{32}S_2 + {}^{13}C^{32}S_2$ experiment (Figure 2, trace c). A similar triplet at 909.0, 906.6, and 900.4 cm^{-1} was observed in the mixed $^{12}C^{32}S_2 + {}^{12}C^{34}S_2$ experiment (Figure 2, trace e). These triplet isotopic structures in the mixed

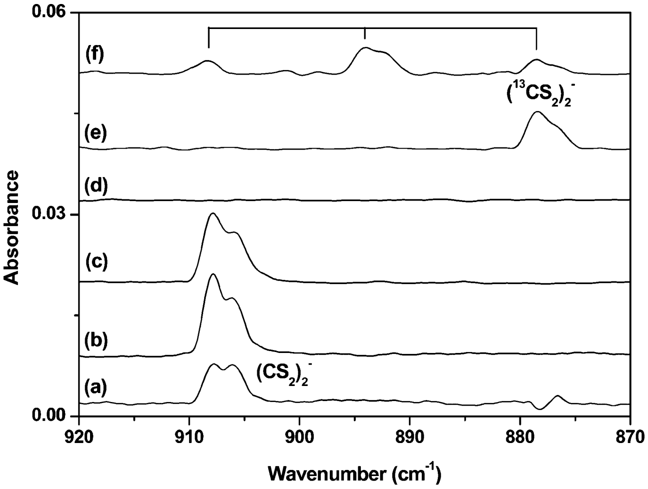

Figure 3. Infrared spectra in the 920−870-cm^{-1} region from condensation of high-frequency discharged CS_2/Ar mixture at 4 K. (a) 1.0% $^{12}C^{32}S_2$, after 1 h of sample deposition, (b) after 15 min of $\lambda > 400$ nm irradiation, (c) after 25-K annealing, (d) after 15 min of $\lambda > 290$ nm irradiation, (e) 0.8% $^{13}CS_2$, after 15 min of $\lambda > 400$ nm irradiation, and (f) 0.5% $^{12}C^{32}S_2$ + 0.5% $^{13}C^{32}S_2$, after 15 min of $\lambda > 400$ nm irradiation.

experiments indicate that the new species has C_2S_4 stoichiometry and involves two equivalent CS_2 subunits. The new species is photosensitive, as the 909.0-cm^{-1} band increased on $\lambda > 400$ nm irradiation and was almost destroyed on $\lambda > 290$ nm irradiation. The 909.0-cm^{-1} band is strong in higher CS_2 concentration experiments when the CS_2^- absorption is very weak. In lower concentration experiments, the CS_2^- absorption is strong and the 909.0-cm^{-1} band is very weak on sample deposition, but increased markedly on $\lambda > 400$ nm irradiation when the CS_2^- absorption was destroyed. Note that the $(CS_2)_2^+$ absorption is strong in higher CS_2 concentration experiments when the CS_2^+ absorption is weak, and in lower concentration experiments the $(CS_2)_2^+$ absorption is weak and increased on annealing when the CS_2^+ is strong. The 909.0-cm^{-1} band cannot be recovered on annealing after broadband irradiation when the other charged species such as CS_2^-, CS_2^+, and $(CS_2)_2^+$ were not present. All of these observations strongly suggest the assignment of the 909.0-cm^{-1} band to the $(CS_2)_2^-$ anion.

A similar band was observed at 908.0 cm^{-1} in solid argon (Figure 3, traces a−d). This band increased on $\lambda > 400$ nm irradiation and disappeared on $\lambda > 290$ nm irradiation and is strongly concentration dependent. The $^{13}C^{32}S_2$ counterpart was observed at 878.4 cm^{-1}, and gave the $^{12}C/^{13}C$ isotopic frequency ratio of 1.0337, about the same as that in solid neon. The mixed $^{12}C^{32}S_2$ + $^{13}C^{32}S_2$ experiment (Figure 3, trace f) revealed a triplet at 908.0, 894.2, and 878.4 cm^{-1}, again characteristic of the participation of two equivalent CS_2 subunits and confirming the $(CS_2)_2^-$ anion assignment.

The structure and electronic configurations of the low-lying states of $(CS_2)_2^-$ have been the subject of considerable experimental and theoretical studies.[1−8] The photodissociation experiments suggest that the most stable form of $(CS_2)_2^-$ contains a C_2S_2 ring and is not the CS_2^-−CS_2 ion−molecule complex.[3] This cyclic form of the anion had been predicted to be 0.6 eV more stable than the complex on the basis of earlier ROHF/6-31G calculations.[1] Recent MP2/6-31+G* theoretical calculations also found the cyclic form to be the most stable structure of the anion,[7] but B3LYP/6-31+G* calculations predicted that the most stable structure has a planar C−C bonded structure with D_{2h} symmetry.[8]

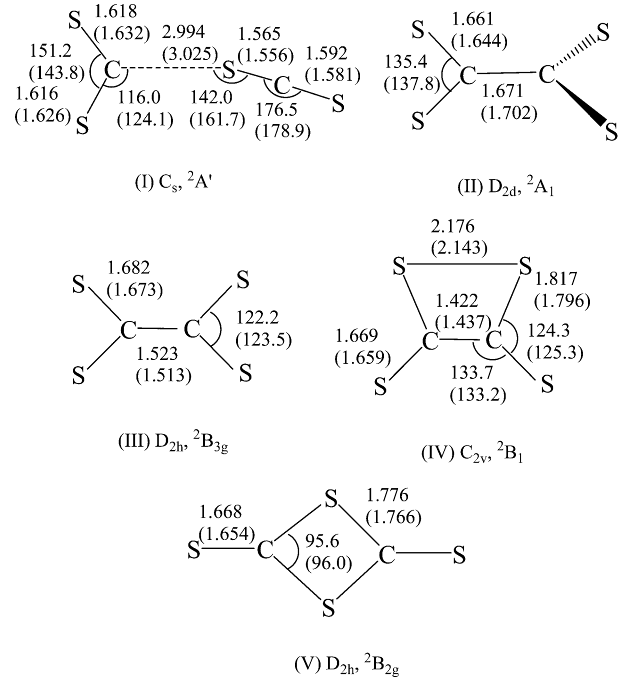

Figure 4. Optimized structures (bond lengths in angstroms, bond angles in degrees) of the stable forms of $(CS_2)_2^-$ anion at the B3LYP/6-311+G* and MP2/6-311+G* (values in parentheses) levels.

TABLE 1: Calculated Energies (E_{Tol}, in Hartree), Relative Energies (E_R in kcal/mol, Relative to the Sum of Separated CS_2 and CS_2^-) and Vertical Detachment Energy (VDE, in eV) of the $(CS_2)_2^-$ Isomers

	B3LYP			MP2	
	E_{Tol}[a]	E_R	VDE	E_{Tol}[b]	E_R
C_s, ^2A	−1669.127 157	−8.9	1.64	−1666.681 377	−8.7
D_{2d}, $^2A_1$	−1669.119 628	−4.1	4.12	−1666.691 875	−15.3
D_{2h}, $^2B_{3g}$	−1669.138 536	−16.0	3.56	−1666.708 218	−25.6
C_{2v}, $^2B_1$	−1669.131 804	−11.8	2.89	−1666.696 394	−18.2
D_{2h}, $^2B_{2g}$	−1669.114 718	−1.1	2.05	−1666.686 349	−11.9

[a] After zero point energy correction. [b] Without zero point energy correction.

To provide additional insight into the spectroscopic assignment of $(CS_2)_2^-$ and to provide a prediction of its structure, we carried out theoretical calculations at both the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. The optimized structures of stable $(CS_2)_2^-$ at both levels of theory are shown in Figure 4. The energies, relative energies with respect to the separated CS_2 and CS_2^-, and the associated vertical detachment energies are listed in Table 1. The calculated vibrational frequencies and intensities at B3LYP/6-311+G* level are listed in Table 2. Five stable structure isomers were found at both levels of theory. Structure (I) corresponds to the ion−molecule complex, which was predicted to have a $^2A'$ ground state with C_s symmetry. Structures (II) and (III) are both C−C covalently bound. Structure (II) is nonplanar with D_{2d} symmetry, whereas structure (III) is planar with D_{2h} symmetry. For the valence isoelectronic $(CO_2)_2^-$ anion, the corresponding D_{2d} structure is the most stable form, and the D_{2h} structure is a transition state of that anion.[9,10,25] Structures (I)−(III) have electronic configurations consistent with electron attachment to the LUMO of the neutral van der Waals $(CS_2)_2$ dimer. Structure (IV) involves a C_2S_2 ring with C−C and S−S chemical bonded having C_{2v} symmetry. Anion (IV) has a $^2B_1$ ground state and is the structure previously considered to be the most stable form of the anion.[7]

TABLE 2: Calculated (B3LYP/6-311+G*) Vibrational Frequencies (cm^{-1}) and Intensities (km/mol) of CS_2, CS_2^-, and $(CS_2)_2^-$

	frequency (intensity, mode)
CS_2	1554.0 (690,σ_u), 673.9 (0, σ_g), 397.5 (6, π_u)
CS_2^-	1163.8 (624, b_2), 651.4 (18, a_1), 330.1 (8, a_1)
$(CS_2)_2^-$ (C_s, ${}^2A$)	1471.5 (320, a), 1285.0 (506, a), 640.5 (2, a), 589.9 (656, a), 403.8 (2, a″), 305.6 (167, a), 289.7 (1, a), 241.0 (0, a″), 106.6 (1, a), 82.0 (9, a), 33.4 (1, a″), 23.0 (1, a)
$(CS_2)_2^-$ (D_{2d}, ${}^2A_1$)	1081.3 (352, e), 729.7 (137, b_2), 653.6 (0, a_1), 490.9 (32, e), 446.3 (0, a_1), 375.6 (16, b_2), 208.1 (0, a_1), 172.6 (10, e), 80.1 (0, b_1)
$(CS_2)_2^-$ (D_{2h}, ${}^2B_{3g}$)	1098.8 (0, b_{3g}), 1062.7 (0, a_g), 966.4 (167, b_{2u}), 832.1 (1, b_{1u}), 634.8 (0, b_{2g}), 489.4 (0, a_g), 338.8 (0, b_{3u}), 332.7 (0, b_{3g}), 283.7 (68, b_{1u}), 244.3 (0, a_g), 45.5 (0, a_u), 42.0 (13, b_{2u})
$(CS_2)_2^-$ (C_{2v}, ${}^2B_1$)	1341.6 (24, a_1), 1045.4 (111, b_2), 844.5 (230, a_1), 670.7 (4, b_2), 530.6 (0, a_2), 476.2 (4, a_1), 378.4 (14, b_2), 373.8 (1, a_1), 270.7 (0, b_1), 265.9 (1, b_2), 177.3 (0, a_1), 118.0 (0, a_2)
$(CS_2)_2^-$ (D_{2h}, ${}^2B_{2g}$)	1149.7 (0, a_g), 1026.7 (643, b_{1u}), 781.3 (44, b_{2u}), 735.4(0, b_{3g}), 559.9 (0, a_g), 441.6 (41, b_{1u}), 378.1 (0, a_g), 366.0 (10, b_{3u}), 279.0 (0, b_{3g}), 210.6 (0, b_{2g}), 173.6 (1, b_{2u}), 102.8 (3, b_{3u})

TABLE 3: Comparison of Observed and Calculated (Unscaled) Vibrational Frequencies (cm^{-1}) of Various $(CS_2)_2^-$ Isotopomers

	Ne	Ar	Cal.
$(CS_2)_2^-$	909.0	908.0	966.4
$({}^{13}CS_2)_2^-$	879.3	878.4	937.1
$({}^{12}CS_2{}^{13}CS_2)^-$	894.9	894.2	949.5
$(C^{34}S_2)_2^-$	900.4		959.9
$(C^{32}S_2C^{34}S_2)^-$	906.6		963.1

Structure (V) has D_{2h} symmetry with a four-membered ring consisting of four equivalent C−S bonds.

According to our B3LYP/6-311+G* and MP2/6-311+G* calculations, the most stable structure of $(CS_2)_2^-$ has planar D_{2h} symmetry (structure (III)). The cyclic form with C_{2v} symmetry (structure (IV)) was predicted to be 4.2 (B3LYP) or 7.4 kcal/mol (MP2) higher in energy than the planar D_{2h} structure. As listed in Table 2, our B3LYP frequency calculations predicted a strong antisymmetric CS_2 stretching vibration (B_{2u} mode) at 966.4 cm^{-1} for the most stable D_{2h} form of $(CS_2)_2^-$. This mode was predicted to be the most intense IR absorption of the anion (167 km/mol). All the other modes in our spectral range (5000−400 cm^{-1}) were predicted to be IR inactive or to have very low IR intensities (less than 1 km/mol). The calculated isotopic shifts also matched the observed values very well (Table 3), which also supports the assignment of the observed vibration to the $(CS_2)_2^-$ anion with D_{2h} symmetry. None of the other four structural isomers was computed to have infrared spectral features that match the observed frequencies. For instance, the C_{2v} structure (structure (IV)) of the anion was predicted to have two strong vibrational modes at 1045.4 cm^{-1} (b_2, 111 km/mol) and 844.5 cm^{-1} (a_1, 230 km/mol). The ion−molecule complex (structure (I)) was computed to have three intense IR absorptions at 1471.5 cm^{-1} (antisymmetric CS_2 stretching, 320 km/mol), 1285.0 cm^{-1} (antisymmetric CS_2^- stretching, 506 km/mol), and 589.9 cm^{-1} (bending, 656 km/mol).

The most stable ${}^2B_{3g}$ D_{2h} structure of $(CS_2)_2^-$ was predicted to be 16.0 (B3LYP) or 25.6 kcal/mol (MP2) lower in energy than the sum of energies of CS_2 and CS_2^-. These values are near the bond dissociation energy of $(CS_2)_2^-$ measured in the gas phase.[1] This suggests that the $(CS_2)_2^-$ anion formed in the gas-phase $CS_2 + CS_2^-$ reaction has a D_{2h} structure. The photoelectron spectrum of $(CS_2)_2^-$ at a photon energy of 4.66 eV exhibited four features at electron-binding energies of 1.65, 2.7, 3.2, and 3.7 eV.[2] The vertical detachment energy of the D_{2h} $(CS_2)_2^-$ anion was computed to be 3.56 eV (B3LYP). We suggest that the 3.7 eV peak observed in the photoelectron spectrum is due to the ${}^2B_{3g}$ D_{2h} $(CS_2)_2^-$ anion.

In previous pulsed-laser ablation experiments with metals and carbon dioxide, the $(CO_2)_2^-$ anions were formed via the $CO_2^- + CO_2$ association reaction in solid matrixes on annealing.[9,10] In present experiments, the $(CS_2)_2^-$ anion absorption does not increase on annealing, suggesting that the anions cannot be formed via the analogous $CS_2^- + CS_2$ association reaction in solid matrixes without activation energy.[12] The $(CS_2)_2^-$ anion absorption increased on $\lambda > 400$ nm irradiation, during which the CS_2^- absorption was bleached, suggesting that $(CS_2)_2^-$ can be formed in solid matrixes through exothermic electron capture by the $(CS_2)_2$ van der Waals dimer. Electrons were produced from photoinduced detachment from other anions with lower electron affinity, such as CS_2^-. The $(CS_2)_2^-$ anion absorption was observed on sample deposition in higher CS_2 concentration experiments, suggesting that the anions can also be formed during the condensation process.

Previous studies have shown that there are several stable structural isomers coexisting in the gas phase.[2,6] Only the most stable structural isomer was trapped in a low-temperature matrix. The other stable isomers observed in the gas phase could either rearrange to the most stable D_{2h} form during the deposition process or were in too low a concentration to be detected by infrared absorption spectroscopy. The present experiments employed a very low power level of discharge, which may favor the formation of the most stable structure.

The CO_2 and CS_2 molecules are isovalent. The neutrals are linear, and their anions are bent. Their dimer anions exhibited significantly different structures. The $(CO_2)_2^-$ anion has a nonplanar D_{2d} structure, whereas the most stable form of $(CS_2)_2^-$ anion has a planar D_{2h} symmetry. Both the dimer anions are chemically bonded species, but the $(CS_2)_2^-$ anion is more strongly bound than the $(CO_2)_2^-$ anion. The C−C bond of $(CO_2)_2^-$ is a half-order chemical bond between the two CO_2 subunits, the bond length was predicted to be 1.985 Å at the B3LYP/6-311+G* level. The C−C bond of $(CS_2)_2^-$ is a single bond with a bond length of 1.523 Å calculated at the B3LYP/6-311+G* level, which is significantly shorter than that of $(CO_2)_2^-$.

Conclusions

One structural isomer of $(CS_2)_2^-$ anion has been studied by matrix isolation infrared absorption spectroscopy and quantum chemical calculations. The $(CS_2)_2^-$ anion was produced by condensation of high-frequency discharged CS_2 in excess neon and argon. On the basis of isotopic substitution experiments, photosensitive absorptions at 909.0 cm^{-1} in neon and 908.0 cm^{-1} in argon are assigned to the antisymmetric CS_2 stretching vibrational mode (b_{2u}) of the $(CS_2)_2^-$ anion, which was predicted to have a C−C chemically bonded planar D_{2h} structure. The anion was formed through exothermic electron capture by the

$(CS_2)_2$ van der Waals dimer during the condensation process as well as in solid matrixes.

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