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Ultraviolet absorption spectrum of cyclic CS_2 in solid Ar

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Abstract

Linear CS_2 dispersed in solid Ar was irradiated with an excimer laser at 193 nm to form *cyc*-CS_2 of which infrared (IR) identification and theoretical calculations were reported previously. We recorded an ultraviolet (UV) absorption spectrum with two progressions (330–380 nm) that correlate well with variations in intensities of IR absorption of *cyc*-CS_2 upon photolysis of linear CS_2 at various stages; hence we assign it to electronic transitions of *cyc*-CS_2. Based on theoretical calculations and vibronic symmetry, we tentatively assign progression A to transition $2^1B_2 \leftarrow X^1A_1$ and progression B to $2^1B_1 \leftarrow X^1A_1$ of *cyc*-CS_2. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon disulfide is an important sulfur compound in the troposphere. Chin and Davis [1] indicate that about 0.57 MT of carbon disulfide is released to the atmosphere each year, about two-thirds of which emanates from various chemical industrial processes and about one-third from marine photosynthetic processes. In its most stable form carbon disulfide has a linear equilibrium conformation, denoted SCS. Electronic excitation of SCS is typically accompanied by substantial alteration of bond length and bond angle. Recently carbon disulfide in a cyclic form, denoted *cyc*-CS_2, was produced on irradiation of SCS isolated in solid N_2 or Ar at 13 K with light at 193 nm from an ArF excimer laser; infrared (IR) absorption lines at 881.3 and 520.9 cm^{-1} were assigned to *cyc*-CS_2 in a N_2 matrix based on isotopic substitution experiments and theoretical calculations [2]. According to theoretical calculations, *cyc*-CS_2 has an S–S bond of length ~2.14 Å and a SCS angle ~76°; its C–S bonds (~1.74 Å) are elongated relative to those of SCS (~1.56 Å). Although *cyc*-CS_2 lies ~73 kcal mol^{-1} above SCS, once formed it is relatively stable. An asymmetric transition structure connecting SCS and *cyc*-CS_2 correlates with a barrier for ring-opening ~24.4 kcal mol^{-1}, corrected for zero-point energy. Conversion of *cyc*-CS_2 to SCS is observed upon further irradiation of the sample with a laser at several wavelengths shorter than 600 nm.

Carbon disulfide belongs to a special class of triatomic molecules characterized by 16 valence electrons. According to molecular orbital theory, the highest occupied molecular orbitals of a linear triatomic species containing 16 valence electrons are degenerate and have π_g symmetry, whereas the lowest unoccupied molecular orbitals have π_u symmetry [3]. Upon deformation to an angular

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conformation, these π_g orbitals split into orbitals of symmetries a_2 and b_2; the energy of the latter increases greatly as the angle decreases from 180°. In contrast, the π_u orbitals split into a_1 and b_1 of which the former decrease in energy as the angle decreases; near an angle $\angle SCS = 90°$ the energies of these orbitals have an order $a_2 < a_1 < b_2 < b_1$. As a result, differences between energies of low-lying electronic states of *cyc*-CS_2 are expected to be smaller than for SCS, and an absorption spectrum to the first electronically excited state of *cyc*-CS_2 might then lie at wavelengths greater than that for SCS.

Spin-allowed transitions $A^1A_2 \leftarrow X^1\Sigma_g^+$ [4] and $B^1B_2 \leftarrow X^1\Sigma_g^+$ [5,6] of SCS produce absorption in a region 290–340 nm; hence absorption of *cyc*-CS_2 is expected to lie in a region with $\lambda > 340$ nm. We report here observation of an electronic absorption spectrum in the region 330–380 nm attributed to *cyc*-CS_2 isolated in solid Ar.

2. Experiments

The experimental setup is similar to that described previously [7,8]. The system is designed so that IR and ultraviolet (UV) absorption spectra can be recorded with the same matrix sample. The matrix support was a platinum-plated copper mirror maintained at 13 K with an APD closed-cycle refrigerator. Matrix samples were prepared by depositing gas mixtures of SCS in Ar (1/200) onto the matrix support. Typically ~8 mmol of mixture was deposited over a period of 2–3 h. A small proportion of SCS was converted to *cyc*-CS_2 on irradiation of the matrix with light from an ArF excimer laser at 193 nm (~2 mJ, 10 Hz) for 1 h. Secondary photolysis of the sample was performed with a XeCl excimer laser at 308 nm (2–3 mJ, 10 Hz). IR and UV absorption spectra were recorded consecutively with a Fourier transform spectrometer (Bomem DA8.3). IR absorption spectra were recorded with a globar source, a KBr beamsplitter, and a HgCdTe detector (77 K), whereas for measurements of UV absorption spectra, a deuterium lamp, a quartz beamsplitter, and a photomultiplier were employed to cover a spectral range 300–400 nm. Typically 400 scans were collected at a resolution 0.5 cm^{-1}.

SCS (Tedia, >99.9%) and Ar (Spectral Gases, 99.999%) were used without purification except for degassing of SCS at 77 K.

3. Results and discussion

3.1. IR absorption spectra of SCS and cyc-CS_2

Trace A of Fig. 1 shows a partial IR absorption spectrum of SCS isolated in solid Ar after deposition. Intense lines at 1528.2 and 2177.9 cm^{-1} (marked ‘a’) are assigned to the asymmetric CS-stretching (ν_3) mode and the $\nu_1 + \nu_3$ combination mode of SCS, respectively; ν_1 denotes the symmetric CS-stretching mode [9]. Lines observed at 1524.5 and 2165.2 cm^{-1} correspond to the ν_3 and $\nu_1 + \nu_3$ modes of $^{32}SC^{34}S$, respectively. Lines at 1478.4 cm^{-1} (also marked ‘a’) is due to $S^{13}CS$. Irradiation of a matrix sample (SCS/Ar = 1/200) with an ArF laser at 193 nm for 1 h produced new lines attributed to *cyc*-CS_2 [2] at 876.5 (881.1) and 517.7 (523.7) cm^{-1} (marked ‘#’ in Fig. 1, trace B)

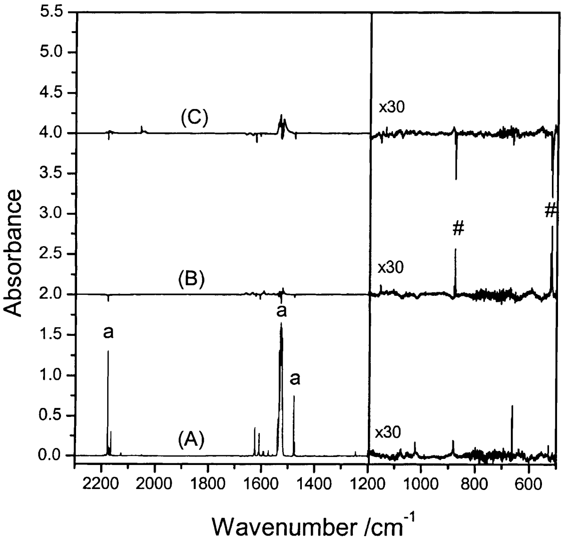

Fig. 1. Partial IR absorption spectrum of a matrix sample of SCS/Ar (1/200) recorded before irradiation (A), difference spectrum recorded after irradiation at 193 nm for 1 h (B), and difference spectrum after further irradiation at 308 nm for 0.5 h (C). The absorbance scale was expanded thirtyfold in a region 1200–500 cm^{-1}. Absorption lines of SCS and *cyc*-CS_2 are marked ‘a’ and ‘#’, respectively.

and a weak line of CS [10,11] at 1270.2 cm^{-1}; wave numbers listed in parentheses are associated with molecules in a minor site. In the difference spectrum, a positive feature indicates its production after irradiation, whereas a negative feature indicates destruction. Lines attributed to SCS decreased only slightly, partly because of saturation in absorption. Observed lines at 876.5 and 517.7 cm^{-1} are assigned to C–S symmetric and asymmetric stretching modes of *cyc*-CS_2; the S–S stretching mode is predicted to be extremely weak and to lie ~498 cm^{-1}, outside our spectral range.

Further irradiation of the matrix sample with laser light at 308 nm for 0.5 h diminished lines of *cyc*-CS_2 nearly completely, whereas lines due to SCS remained nearly unaltered, as illustrated in the difference spectrum in Fig. 1, trace C. We observed no absorption line of C_2S_2 at 1179 cm^{-1} [10,12] that might be formed from dimerization of CS.

3.2. UV absorption spectra of SCS and cyc-CS_2

UV absorption spectra were recorded immediately after recording IR spectra at each stage of photolysis. Absorption features in trace A of Fig. 2 are readily assigned to SCS; the pattern of absorption lines is similar to that of the 'V-system' in the gas phase in a transition assigned as $B^1B_2(^1\Delta_u) \leftarrow X^1\Sigma_g^+$ [4]. Observed origin at 30 777 cm^{-1} and intervals ~585 cm^{-1} are close to values $T_0 = 30\,756$ cm^{-1} and $\nu_2 = 580$ cm^{-1} reported for the $K' = 0(\Sigma)$ component of the B ← X transition in the gas phase. In trace B of Fig. 2, recorded after irradiation of the sample at 193 nm for 1 h, new absorption lines appear in a region 330–380 nm (26 500–30 500 cm^{-1}). These lines appear to belong to two progressions with intervals ~350 and ~570 cm^{-1}; they are labeled as progressions A and B, respectively, in Fig. 2B. Wave numbers of these lines are listed in Table 1; uncertainties estimated to be ±5 cm^{-1} are due to breadth of lines and poor ratio of signal to noise. A weak but sharp feature near 38 545 cm^{-1}, also recorded but not shown, is readily assigned to absorption of CS [10].

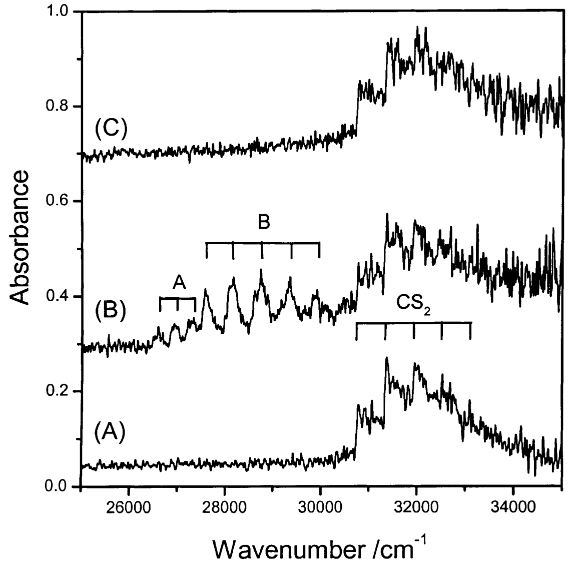

Fig. 2. UV absorption spectrum of a matrix sample of SCS/Ar (1/200) recorded before irradiation (A), after irradiation at 193 nm for 1 h (B), and after further irradiation at 308 nm for 0.5 h (C).

After secondary photolysis at 308 nm of the sample for 0.5 h, the new spectrum in trace B diminished but absorption of SCS remains nearly unaltered. The photolytic behavior of the new spectrum correlates well with that of IR absorption lines of *cyc*-CS_2. Considering possible photolysis products of SCS in solid Ar and observed IR absorption spectra, we attribute the new UV spectrum to *cyc*-CS_2.

The broad width (~200 cm^{-1}) of observed lines in solid Ar and the poor ratio of signal to noise prevent meaningful vibronic analysis of this spectrum using ^{13}C- or ^{34}S-isotopic labeling. Based on the best available spectra, we consider that these two progressions belong to separate electronic transitions because evidence of combination bands involving these two progressions is lacking. The first member of progression B at 27 607 cm^{-1}, appears to be the origin of a transition because its intensity is relatively large and because there is no preceding member of the progression with a suitable interval. Intervals in this progression ranges from 542 to 590 cm^{-1}. Slightly irregular spacing and greater widths for the second to the fourth members of the progression indicate a possible second progression with a slightly smaller interval that overlaps progression B, but further analysis using deconvolution is impractical.

Table 1
Spectral data of observed absorption features attributed to *cyc*-CS_2 in solid Ar

Progression A			Progression B		
Wavelength (nm)	Wave numbers (cm^{-1})	Interval (cm^{-1})	Wavelength (nm)	Wave numbers (cm^{-1})	Interval (cm^{-1})
376.14	26 586	353	362.23	27 607	542
371.21	26 939	348	355.25	28 149	590
366.47	27 287		347.96	28 739	586
			341.01	29 325	557
			334.65	29 882	

Whether the first observed member of progression A, lying at 26 586 cm^{-1}, is the origin of the other transition is unclear because its intensity is small; weakness of a preceding member of this progression might preclude detection. The fourth member of the progression, expected to lie ~27 615 cm^{-1}, nearly coincides with the first member of progression B at 27 607 cm^{-1}.

3.3. Assignments of observed transitions

The geometry, energy, and vibrational wave numbers of *cyc*-CS_2 in its ground X^1A_1 state were previously characterized theoretically [2]. According to density functional calculations with the B3LYP/aug-cc-pVTZ method, *cyc*-CS_2 has an S–S bond of length ~2.14 Å and ∠SCS ≅ 76°; its C–S bonds (~1.74 Å) are longer than those of SCS (~1.56 Å). Electronically excited states of *cyc*-CS_2 have recently been investigated with the full-valence complete-active-space self-consistent-field method, CASSCF(16,12), with an aug-cc-pVTZ basis set; numbers in parentheses indicate that 16 electrons associated with 12 orbitals are active [13]. Subsequent calculations with a multi-reference configuration-interaction (MRCI) method yielded a single-point energy at each optimized structure. According to results from MRCI calculations, the first two groups, states $^1B_1$ and $^1B_2$, of electronically excited singlet states of *cyc*-CS_2 lie ~2.17 and 3.79 eV (or 17 500 and 30 570 cm^{-1}) above the ground X^1A_1 state. In view of possible errors in calculations, observed new transitions correlate better with the second group. States 2^1B_1 and 2^1B_2 are predicted to have energies 3.779 and 3.809 eV, C–S bonds of length 1.724 and 1.828 Å, and angles ∠SCS = 85.1° and 81.3°, respectively. The orders of energies for these two states might be unreliable because such calculations can have large errors and because the orders of energies is reversed with MCSCF calculations. Vibrational wave numbers for each electronically excited state are not accurately predictable with this method. According to vibronic symmetry of C_{2v} molecules, the transition $^1B_1 \leftarrow {}^1A_1$ is expected to have active ν_1 and ν_2 progressions with A_1 symmetry, whereas all three modes are symmetry-allowed for the transition $^1B_2 \leftarrow {}^1A_1$.

Progression B is likely attributed to the $2^1B_1 \leftarrow X^1A_1$ transition for the following reasons. The length of C–S bonds in the 2^1B_1 state is similar to that in the X^1A_1 state; hence the origin is expected to have large intensity. The 2^1B_1 state has a C–S bond shorter than that of the 2^1B_2 state, hence vibrational wave numbers for C–S stretching modes are expected to be greater for the 2^1B_1 state than for the 2^1B_2 state, and indeed progression B has intervals greater than those of progression A. A likely second progression unresolved from progression B might be due to the S–S stretching (ν_2) mode. Progression A is thus tentatively assigned to the $2^1B_2 \leftarrow X^1A_1$ transition because its intervals are smaller, corresponding to a longer C–S bond, and because its origin is less obvious.

IR and UV spectra of C_2S_2 isolated in an Ar matrix were recorded after deposition of a gaseous mixture of CS_2/Ar subjected to electric discharge [10]. Wave numbers of observed lines are 25 523, 25 960, 26 055, 26 497, 26 591, 27 042, and 27 152 cm^{-1}; intervals 532 and 437 cm^{-1} correspond to symmetric terminal C–S stretching (ν_2) and trans bending (ν_4) modes, respectively. Although lying in a similar spectral region, observed spectra in this work do not resemble that of C_2S_2, consistent with results of IR absorption in which no line attributable to C_2S_2 is observed.

4. Conclusion

We have recorded a new UV absorption spectrum comprising two main progressions (A and B) in a spectral region 330–380 nm after irradiation of an Ar matrix containing SCS with lasers. These spectral features show photolytic behavior correlating with IR absorption lines of *cyc*-CS_2 at 876.5 and 517.7 cm^{-1}; they appear upon irradiation at 193 nm and diminish after further irradiation at 308 nm. Based on consideration of molecular symmetry and geometry predicted with theoretical calculations, we tentatively assign progression A to the $2^1B_2 \leftarrow X^1A_1$ transition and progression B to $2^1B_1 \leftarrow X^1A_1$ of *cyc*-CS_2; observed intervals $\sim$350 and 570 cm^{-1} correspond to C–S stretching modes of the upper state. Progression B has an origin at 27 607 cm^{-1} whereas the origin of progression A might lie below 26 586 cm^{-1}.

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