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Matrix Isolation Study of the Infrared Spectrum of Thioformaldehyde[1]

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H_2CS has been trapped in argon and nitrogen matrices at 14 K as a product of the pyrolysis of *s*-trithiane or $(CH_3S)_2$ and of the ultraviolet or vacuum ultraviolet photolysis of CH_3SH. A small concentration of H_2CS has also been observed upon vacuum ultraviolet photolysis of a mixture of CH_4 and H_2S in an argon matrix. The isotopic data support the assignment of absorptions at 993 and at 1063 cm^{-1} to the out-of-plane deformation and the C═S stretching fundamentals of H_2CS. Absorptions in the CH stretching region which were assigned to H_2CS in an earlier gas-phase study were confirmed in the matrix experiments. Studies of the vacuum ultraviolet photolysis of CD_3SH have provided information on the mechanism of the photolysis process.

INTRODUCTION

Until recently, the species thioformaldehyde was known only as its trimer. The monomer was first detected in mass spectrometric studies by Jones and Lossing (*1*) of the pyrolysis of thiacyclobutane. Largely on chemical evidence, Callear and coworkers (*2*, *3*) assigned an absorption band which appeared at 2117 Å on flash photolysis of a variety of sulfur-containing compounds to H_2CS. They noted that this band persisted for several seconds. At about the same time, Johnson and co-workers (*4–6*) published a series of papers reporting the microwave and millimeter wave spectra of H_2CS, produced in good yield by the thermal decomposition of the trimer or of $(CH_3S)_2$. The half-life of H_2CS was estimated to be 6 min at pressures of 10 to 50 × 10^{-3} Torr. Isotopic substitution studies permitted derivation of the complete molecular structure. Subsequently, microwave transitions of H_2CS have been detected in absorption in the direction of the galactic center radio source Sagittarius B2 (*7*, *8*). High-resolution gas-phase infrared studies by Johns and Olson (*9*) of the C–H stretching region in a flow system in which F atoms were used to abstract an H atom from CH_3S have led to the assignment of both C–H stretching fundamentals and of one overtone band of H_2CS. Although Johns and Olson estimated the positions of the lower-frequency vibrational fundamentals of H_2CS, these fundamental absorptions have not heretofore been directly observed. The following discussion summarizes the results of matrix isolation studies designed to provide a more complete characterization of the vibrational spectrum of H_2CS.

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[2] Posthumous contribution.

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EXPERIMENTAL DETAILS[3]

The trimer of H_2CS, *s*-trithiane (Eastman Organic Chemicals), and $(CH_3S)_2$, dimethyldisulfide (Matheson, Coleman, and Bell), used in the pyrolysis experiments were not subjected to further purification. Samples of CH_3SH, CH_4, and H_2S (Matheson Co., Inc.) and of CH_4 (54% ^{13}C), CD_3H, CD_4, and CD_3SH (Merck and Co. Inc.) were used without further purification, as were the argon and prepurified grade nitrogen (Matheson Co., Inc.) used as matrix gases. One experiment was also conducted using CH_3SD, prepared by isotopic exchange of CH_3SH with D_2O followed by drying of the product by passing through a column packed with P_2O_5. Except in the $(H_2CS)_3$ pyrolysis experiments, mixtures of the H_2CS precursor with the matrix gas were prepared using standard manometric procedures.

In studies of the products of pyrolysis of $(H_2CS)_3$, this material, a white solid, was packed into the closed end of a length of quartz tubing, the open end of which had been sealed into a flange using epoxy cement. In turn, this flange was attached to the base of the cryostat, which could be rotated into position for deposition of the pyrolysis products on the cold sample window. A portion of the tube between the sample and the flange was heated using a Meeker burner or a nichrome winding. Conduction of heat to the sample sufficed to vaporize a low pressure of it, which was decomposed in the high-temperature region. In experiments using the nichrome winding, temperatures were estimated by placing a platinum versus platinum-10% rhodium thermocouple in mechanical contact with the quartz tubing. A large excess of argon at a controlled low pressure was mixed with the pyrolysis products through an inlet tube directed coaxially with the sample window.

Because $(CH_3S)_2$ possesses a significant vapor pressure at room temperature, it was possible to prepare $Ar{:}\,(CH_3S)_2 = 100$ samples using standard manometric procedures. These samples were passed at a controlled low pressure through a length of quartz tubing packed with short lengths of quartz rod and heated by an oxygen torch, and the pyrolysis products were rapidly quenched on the cryostat sample window. In some of the experiments, an excess of argon was added to the pyrolysis sample using an auxiliary inlet tube.

Photolysis studies were conducted on normal and isotopically substituted $Ar{:}CH_3SH$, $N_2{:}CH_3SH$, and $Ar{:}CH_4{:}H_2S$ samples. $Ar{:}CH_3SH$ samples of mole ratio ranging from 100 to 400, $N_2{:}CH_3SH = 200$ samples, and $Ar{:}CH_4{:}H_2S = 100{:}1{:}1$ and $200{:}1{:}1$ samples were studied. Significant photodecomposition of matrix-isolated CH_3SH occurred upon exposure of the sample to the full light of a medium-pressure mercury arc. However, much higher yields of photolysis products were obtained when vacuum-ultraviolet photolysis was employed. The hydrogen discharge lamp and the photolysis procedures used in these experiments have previously been described (*10*). In all of the pyrolysis and photolysis experiments, it was found possible to separate the product absorptions into different groups according to their behavior upon subsequent exposure of the sample to the full or filtered light of a medium-pressure mercury arc.

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[3] Certain commerical instruments and materials are identified in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

The cryostats used for the pyrolysis experiments and for some of the photolysis experiments have previously been described (*11*). Most of the vacuum-ultraviolet photolysis experiments were conducted using an Air Products Model CS-202 Displex closed-cycle helium refrigeration system. In these experiments, the sample was deposited on a gold-plated copper surface, and the infrared beam was reflected from this plane surface, using an optical configuration in the spectrometer sample compartment similar to that described by Hastie, Hauge, and Margrave (*12*). The geometry of the helium refrigeration system was such that a considerably greater fraction of the sample than in the cryostat experiments was frozen onto the cold sample surface. This factor, together with the enhanced absorption provided by the double traversal of the sample deposit by the reflected beam, dictated a decrease in the rate of sample deposition to approximately 2 mmol/hr, approximately one-third of the rate used for the cryostat experiments.

The infrared spectra of pyrolyzed $(H_2CS)_3$ isolated in argon and nitrogen were recorded on a Beckman IR-20A infrared spectrophotometer. Under the conditions of these experiments, the resolution and frequency accuracy are estimated to be 2 cm^{-1} over the 250–4000 cm^{-1} spectral range of the instrument. The remaining experiments were performed using a Beckman IR-9 infrared spectrophotometer with slit schedule and scanning speed adjusted to give a resolution and frequency accuracy of 1 cm^{-1} between 400 and 2000 cm^{-1} and 2 cm^{-1} between 2000 and 4000 cm^{-1}.

OBSERVATIONS

A suitable vapor pressure of *s*-trithiane for studies of its spectrum isolated in an argon matrix was obtained by heating the solid material to 85° ± 2°C. When the high-temperature region of the quartz tube was maintained at a temperature below about 525°C, the infrared spectrum of the matrix-isolated material showed a very strong peak at 735 cm^{-1} and strong peaks at 910, 1173, and 1400 cm^{-1}, in good agreement with the absorptions reported by Mecke and Spiesecke (*13*) for *s*-trithiane in KBr pellets. Moderately intense absorptions at 1223 and 2900 cm^{-1} also may have been contributed by *s*-trithiane, but their identification is less certain.

As the high-temperature region of the quartz tube was heated above 525°C, thermal decomposition of *s*-trithiane assumed an increasingly important role, and at temperatures above about 700°C thermal decomposition was essentially complete. The most prominent product absorption was that of CS_2, at 1530 cm^{-1}. Also prominent were absorptions at 987 and 1041 cm^{-1}, with essentially constant relative intensities over the temperature range studied in these experiments. Numerous weaker product absorptions also appeared, including peaks assigned to CH_4, C_2H_2, and C_2H_4. When the deposit was exposed to radiation of wavelength shorter than 2800 Å, the 1041 cm^{-1} peak and a number of other less prominent peaks due to unidentified products decreased rapidly in intensity. Although peaks on the shoulders of the very prominent 987 cm^{-1} absorption decreased in intensity, there was very little change in the intensity of the 987 cm^{-1} peak itself. The 1276 cm^{-1} absorption of CS (*14*) appeared on irradiation of the sample.

The absorptions observed below 1500 cm^{-1} for unpyrolyzed samples of $(CH_3S)_2$ isolated in an argon matrix agree very well with prominent infrared peaks in the spectrum of liquid $(CH_3S)_2$, reported by Trotter and Thompson (*15*). Weak to moderately intense absorptions at 2826 and 2859 cm^{-1} and stronger absorptions at 2934 and 2998 cm^{-1} may also be assigned to $(CH_3S)_2$, not previously studied in this spectral region.

A rich spectrum was also obtained on pyrolysis of $(CH_3S)_2$, but the products were quite different from those characteristic of the pyrolysis of *s*-trithiane. Absorptions of CH_3, CH_4, and CS_2 were readily identified. Of the remaining product absorptions, only those at 988 and 2980 cm^{-1} corresponded with product absorptions characteristic of pyrolyzed *s*-trithiane samples, which suggests that, if H_2CS is common to both systems, the 988 and/or 2980 cm^{-1} absorptions are contributed by it. Since in the $(CH_3S)_2$ experiments the 2980 cm^{-1} absorption was considerably more prominent than the 988 cm^{-1} absorption, whereas in the *s*-trithiane experiments the reverse was true, more than one product must contribute to one of these absorptions.

On mercury-arc photolysis of Ar: CH_3SH samples of mole ratio between 100 and 400, very prominent absorptions of CS_2 and CH_4 appeared. The 1276 cm^{-1} absorption of CS and its satellite at 1272 cm^{-1} were also present, and the 1276 cm^{-1} peak was extremely prominent in the experiment at mole ratio 400, indicating that extensive photodecomposition of the sample occurred. A moderately intense pair of product absorptions also appeared at 988 and 994 cm^{-1}, and weaker photolysis product absorptions were observed at 1057 and 2970 cm^{-1}.

A much richer product spectrum was observed on vacuum ultraviolet photolysis of CH_3SH isolated in an argon matrix. The absorptions characteristic of the unphotolyzed and photolyzed deposits, respectively, are summarized in the first two columns of Table I, and spectral regions of especial interest are shown in Fig. 1. With allowance for small matrix shifts, the absorptions reported for the initial deposit lie close to those reported by May and Pace (*16*) for CH_3SH, except that the SH stretching fundamental was too weak to be observed in the sample deposits employed for these experiments. As in the mercury-arc photolysis studies, the absorptions of CH_4, CS, and CS_2 were prominent in the spectra of photolyzed samples. Typically, the 1529 cm^{-1} absorption of $^{12}CS_2$ was so prominent that the corresponding absorption (at 1479 cm^{-1}) of $^{13}CS_2$ present in 1% natural abundance could be detected. The 988, 993, 1057, and 2970 cm^{-1} absorptions were considerably more prominent than in the mercury-arc photolysis studies. When the deposit was exposed to radiation of wavelength shorter than 2800 Å, these four absorptions, a weak 1063 cm^{-1} shoulder on the CH_3SH absorption, a weak, broad absorption at 1753 cm^{-1}, weak absorptions at 2874 and 2962 cm^{-1}, and a shoulder at 3028 cm^{-1} grew markedly in intensity. The absorption of CH_4 at 1305 cm^{-1} also grew in intensity under these conditions, but the increase in its intensity was considerably less marked than was that of the other absorptions. As shown in Table I, there were several other types of behavior of product absorptions on mercury-arc irradiation. Absorptions of CS_2 and of OCS grew in intensity on exposure of the sample to either radiation of wavelength greater than 2800 Å or radiation in the 4200–2300 Å spectral range. A prominent absorption at 424 cm^{-1} and its satellite at 431 cm^{-1} were unique in growing significantly in intensity on exposure of the sample to radiation of wavelength greater than 2800 Å but disappearing after exposure of the sample to shorter wavelength radiation. Absorptions at 805, 816, and 1397 cm^{-1} diminished in intensity on exposure of the sample even to long wavelength radiation. The very prominent CS absorption and its satellite also tended to diminish somewhat in intensity under these conditions. Weak absorptions at 1179 and 1419 cm^{-1} were unchanged when the sample was exposed

Table I

Absorptions[(a)] (cm^{-1}) Observed in Studies of the Vacuum Ultraviolet Photolysis of Ar:CH_3SH Samples at 14°K and Their Behavior on Subsequent Filtered Mercury-Arc Irradiation

Initial Deposit	H Photolysis	Hg Photolysis		Assignment
		λ>2800 Å	4200>λ>2300 Å	
	424 s	+	-	
	431 m,sh	+	-	
	554 vw	+	+	
704 m				
800 m				
	805 w-m	-	-	
	816 m-s	-	-	
956 s				
	988 m-s	0	+	H_2CS
	993 s	0	+	H_2CS
	1056 w	0	+	H_2CS
	1063 w,sh	0	+	H_2CS
1069 s				
	1179 w	0	-	
	1273 sh	-	-	CS
	1276 vs	0	-	CS
	1305 vs	0	+	CH_4
1328 s				
	1397 w-m	-	-	
	1419 w	0	-	
1438 s				
1448 s				
	1479 w	0	+	$^{13}CS_2$
	1529 vs	+	+	$^{12}CS_2$
	1753 w,br	0	+	
	2052 vw	+	+	OCS
	2180 w	+	+	CS_2
2856 m				
	2874 w	0	+	H_2CS
2938 sh				
2950 s				
	2962 w	0	+	H_2CS
	2970 w-m	0	+	H_2CS
3008 s				
3014 sh				
	3028 sh	0	+	CH_4, H_2CS

[(a)] vw--very weak; w--weak; m--medium; s--strong; vs--very strong; sh--shoulder; br--broad. +, 0, - designate change in relative intensity on exposure of sample to filtered mercury-arc radiation.

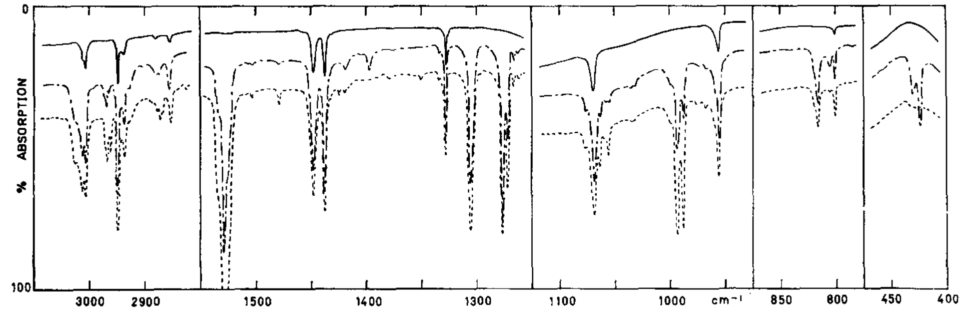

FIG. 1. Ar:CH_3SH = 200. 14 K. ——, 5.3 μmol CH_3SH, unphotolyzed; — — —, 37.4 μmol additional CH_3SH deposited over period of 253 min with concurrent photolysis by hydrogen discharge radiation; - - - -, 120 min subsequent mercury-arc photolysis, 4200 > λ > 2300 Å.

to radiation of wavelength longer than 2800 Å but diminished in intensity when the sample was exposed to shorter wavelength radiation.

Nitrogen-matrix experiments yielded results which were, in general, similar to those of the argon-matrix ones. The pairs of absorptions at 988 and 993 cm^{-1}, at 1056 and 1063 cm^{-1}, and at 2962 and 2970 cm^{-1} characteristic of the argon-matrix experiments were replaced by single absorptions at 995, 1062, and 2973 cm^{-1} in the nitrogen-matrix studies. The 424 and 431 cm^{-1} absorptions were also replaced by a single very strong absorption at 436 cm^{-1}, which suggests that the splittings characteristic of these absorptions in an argon matrix resulted from the trapping of the product molecules in distinct types of sites in the argon lattice. Also of interest was the appearance of a moderately intense absorption due to CH_3 (*10*) at 611 cm^{-1} in the nitrogen-matrix experiments.

One study of the mercury-arc photolysis of an Ar: CH_3SD sample was also conducted, using a barium fluoride cryostat window, which permitted access of relatively short wavelength ultraviolet radiation to the sample but precluded observation of the infrared spectrum below about 800 cm^{-1}. The appearance of prominent CH_3SD absorptions at 960 and 1004 cm^{-1}, close to fundamental absorptions reported by May and Pace (*16*) for this molecule, but of only weak absorptions at 956 and 1069 cm^{-1}, contributed by the corresponding fundamentals of CH_3SH, indicated that a high degree of deuterium substitution on the sulfhydryl group had been achieved. Nevertheless, upon photolysis moderately intense absorptions appeared at 988 and 993 cm^{-1}, unshifted from the product absorptions characteristic of the undeuterated sample. A weak product absorption also appeared at 893 cm^{-1}, the absorptions of CS and of CS_2 were prominent, and absorptions of CH_3D were recognized at 1155, 1305, and 2196 cm^{-1}.

The appearance of absorptions near 990 and 2970 cm^{-1} in the pyrolysis experiments, in which H_2CS was known to be a product, and in the studies of the ultraviolet and vacuum ultraviolet photolysis of CH_3SH, in which the formation of H_2CS would also be expected to occur, suggests the assignment of these two absorptions to this product; no other unassigned product absorptions are common even to any two of these three experimental systems. Furthermore, in the vacuum-ultraviolet photolysis experiments weaker absorptions attributable to this same product appeared at 2874 and 3028 cm^{-1}. These absorptions, together with that at 2970 cm^{-1}, may be compared to the absorptions at 2877, 2971, and 3025 cm^{-1} assigned to gas-phase H_2CS by Johns and Olson (*9*). Although these arguments provide a strong case for the assignment to H_2CS of the absorptions near 990 cm^{-1} and of the other absorptions which behave similarly on secondary photolysis, further isotopic data would be extremely valuable, not only to provide additional support for the identification, but also to yield information on the vibrational assignment. As is shown in the solid trace (a) of Fig. 2, several weak to moderately intense absorptions appeared between 750 and 1000 cm^{-1} on vacuum-ultraviolet photolysis of an $Ar:CH_4:H_2S = 100:1:1$ sample during deposition. On subsequent mercury-arc photolysis of the total deposit, the 993 cm^{-1} absorption and its shoulder at 988 cm^{-1} grew significantly in intensity, whereas the other absorptions were unchanged or diminished in intensity. It was concluded that H_2CS was formed in small concentration in this system and that it might be possible to obtain further isotopic substitution data for the 993 cm^{-1} absorption. Trace (b) of Fig. 2 shows the result of another experiment in which the methane was enriched to 54% in carbon-13. A weak pair of absorptions appeared at 993.0 and 984.8 cm^{-1}. When an expanded scale was used, the growth in these absorptions on subsequent mercury-arc photolysis was ap-

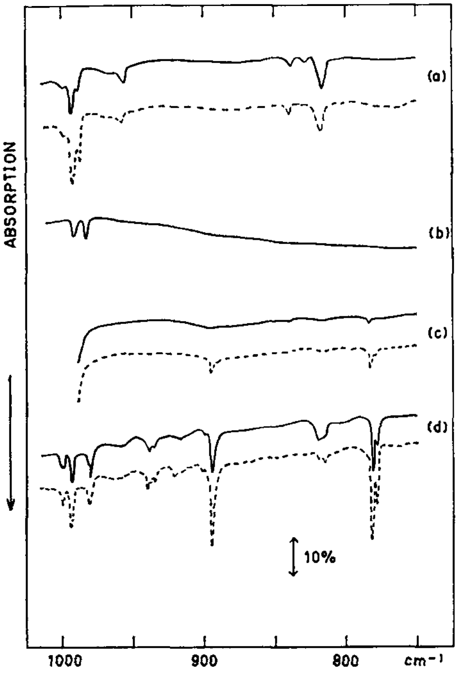

FIG. 2. (a) $Ar:CH_4:H_2S = 100:1:1$. 14 K. ——, 79.2 μmol CH_4, H_2S deposited over period of 353 min with concurrent photolysis by hydrogen discharge radiation; – – – –, 120 min subsequent mercury-arc photolysis, $4200 > \lambda > 2300$ Å. (b) $Ar:CH_4$ (54% ^{13}C)$:H_2S = 100:1:1$. 14 K. ———, 186 μmol CH_4, H_2S deposited over period of 319 min with concurrent photolysis by hydrogen discharge radiation. (c) $Ar:CD_4:H_2S = 200:1:1$. 14 K. ——, 33.7 μmol CD_4, H_2S deposited over period of 313 min with concurrent photolysis by hydrogen discharge radiation; – – – –, 75 min subsequent mercury-arc photolysis, $4200 > \lambda > 2300$ Å. (d) $Ar:CD_3SH = 200$. 14 K. ——, 45.5 μmol CD_3SH deposited over period of 275 min with concurrent photolysis by hydrogen discharge radiation; – – – –, 248 min subsequent mercury-arc photolysis, $4200 > \lambda > 2300$ Å.

parent. In studies of $Ar:CD_4:H_2S$ samples which had been deposited with concurrent hydrogen-discharge photolysis, very weak absorptions appeared at 895 and 783 cm^{-1}. As is shown in traces (c) of Fig. 2, these two absorptions, barely present after the initial photolysis, grew significantly on mercury-arc irradiation of the sample. Although these product peaks were weak, their positions were confirmed in several photolysis experiments. It may be noted again that a weak peak appeared at 893 cm^{-1} in the study of the mercury-arc photolysis of an $Ar:CH_3SD$ sample.

A series of experiments, the results of which are summarized in Table II, was also conducted on the vacuum-ultraviolet photolysis of $Ar:CD_3SH$ samples. The 750–1000 cm^{-1} spectral region of a typical sample, deposited with concurrent hydrogen-discharge photolysis, is shown in traces (d) of Fig. 2. The 783 and 895 cm^{-1} peaks were greatly enhanced in this system, and again they grew on subsequent mercury-arc irradiation of the sample, providing still further support for their assignment to D_2CS and HDCS, respectively. An absorption at 994 cm^{-1} also grew somewhat on mercury-arc irradiation of the sample. Although this absorption may be contributed at least in

Table II

Absorptions(a) (cm^{-1}) Observed in Studies of the Vacuum Ultraviolet Photolysis of $Ar:CD_3SH$ Samples at 14°K and Their Behavior on Subsequent Filtered Mercury-Arc Irradiation

Initial Deposit	H Photolysis	Hg Photolysis		Assignment
		λ>2800 Å	4200>λ>2300 Å	
	454 w			CD_3
	543 w-m	-	-	
	617 w	-	-	
	623 m	-	-	
	625 m	-	-	
642 w-m				
	699 vw		+	
724 w				
	779 sh	+	+	D_2CS
	783 m	+	+	D_2CS
	815 w-m	-	-	
	819 w-m	-	-	
	895 m	+	+	HDCS
	936 vw		0	
	939 vw		0	
	941 vw		+	
980 w-m				
	994 w-m	+	+	CD_4

Table II--Continued

Initial Deposit	H Photolysis	Hg Photolysis.		Assignment
		$\lambda>2800$ Å	$4200>\lambda>2300$ Å	
	1001 w		+	CD_3H
1016 w-m				
	1029 w-m,br		+	CD_3H
1047 m				
1055 m				
	1168 vw		+	
	1174 vw		+	
	1182 vw		+	
	1261 w,sh			
	1265 w-m		-	
	1272 s,sh	+	-	CS
	1276 vs	+	-	CS
	1281 sh		-	
	1288 w-m		+	CD_3H
	1300 w		-	
	1305 w		-	
	1330 w			
	1355 w		0	
	1400 w,br		+	HDO
	1479 w		+	$^{13}CS_2$
	1529 vvs		+	$^{12}CS_2$
	1648 w-m		-	

part by H_2CS, the rather prominent 988 cm^{-1} satellite absorption of H_2CS was not present, and the assignment of the 994 cm^{-1} absorption to CD_4, also expected to grow on mercury-arc irradiation of the sample, seems appropriate. In contrast to the results given in Table I, some growth in the absorptions attributed in Table II to D_2CS and to HDCS was observed even on exposure of the sample to radiation of wavelength longer than 2800 Å. However, the growth in the intensity of these absorptions was much more marked when radiation of shorter wavelengths was employed. Also present were the very prominent absorptions of CS and of CS_2, a rather prominent OCS absorption at 2050 cm^{-1}, and several absorptions of CD_3H, at 1001, 1029, 1288, and 2140 cm^{-1}. The counterpart of the 424–431 cm^{-1} pair of absorptions of the Ar:CH_3SH photolysis experiments was not observed, presumably because it was shifted below the 400 cm^{-1} cutoff of the spectrometer. On the other hand, a weak absorption at 454 cm^{-1} could be assigned to CD_3 (*10*), whereas in the studies of undeuterated samples the CH_3 absorption

Table II--Continued

Initial Deposit	H Photolysis	Hg Photolysis		Assignment
		$\lambda>2800$ Å	$4200>\lambda>2300$ Å	
	1737 w-m		+	
	1742 w-m		0	
	2050 s	+	+	OCS
	2054 sh	+	+	OCS
	2088 w-m	+	0	
	2140 m	0	0	CD_3H, CO
2146 w-m				
	2157 w		+	
	2178 w-m			CS_2
	2232 vw			
2260 w				

[a] vw--very weak; w--weak; m--medium; s--strong; vs--very strong; sh--shoulder; br--broad. +, 0, - designate change in relative intensity on exposure of sample to filtered mercury-arc radiation.

could be detected only in nitrogen matrix studies. The detection of CD_3, but not of CH_3, in the argon-matrix experiments is attributed to the relative sharpness of the CD_3 absorption, with its compressed rotational structure. Moderately strong absorptions at 543, 623, 625, 815, and 819 cm^{-1} diminished in intensity on exposure to either wavelength range of mercury-arc radiation, as did the absorptions at 805, 816, and 1397 cm^{-1} of the Ar:CH_3SH photolysis experiments. The remaining absorptions were weak, and information on their secondary photolysis behavior is fragmentary.

In studies of photolyzed N_2:CD_3SH samples, a strong product absorption appeared at 784 cm^{-1} and a moderately intense absorption at 897 cm^{-1}. These two absorptions and a weak to moderately intense absorption at 939 cm^{-1} grew on subsequent ultraviolet irradiation of the sample. The 463 cm^{-1} absorption characteristic of CD_3 in a nitrogen matrix and the 517 cm^{-1} absorption characteristic of CHD_2 in a nitrogen matrix (*10*) were both moderately intense. The 543 cm^{-1} absorption observed in photolyzed Ar:CD_3SH samples was not present. In general, the product absorptions at higher frequencies behaved similarly to their counterparts in the argon-matrix experiments.

DISCUSSION

Vibrational Spectrum of H_2CS

As previously noted, the appearance of the 993 cm^{-1} absorption in the pyrolysis experiments, in which H_2CS is known to be a product, and in the photolysis studies, in which H_2CS is expected to be produced, strongly suggests the assignment to H_2CS of this absorption and of the other absorptions with similar photolytic behavior. Among these absorptions are peaks at 2874, 2970, and 3028 cm^{-1}, close to the band centers of absorptions assigned by Johns and Olson (*9*) to gas-phase H_2CS. As is shown by the calculations summarized in Table III, the isotopic substitution studies are also consistent with this assignment. In the absence of isotopic data and of the data of Johns and Olson, the 993 cm^{-1} absorption might reasonably be assigned to the C═S stretching fundamental, the in-plane CH_2 wagging fundamental (HCS deformation), or the out-of-plane deformation fundamental of H_2CS. A fourth possible assignment, to the totally symmetric CH_2 "scissors" fundamental, is unlikely; the corresponding fundamental of the closely related species H_2CO appears near 1500 cm^{-1}. The relatively small carbon-13 shift and the large deuterium shifts in the 993 cm^{-1} absorption are inconsistent with its assignment as the C═S stretching fundamental. Using the Wilson *GF*-matrix formalism (*17*), the H_2CS structure determined by Johnson, Powell, and Kirchhoff (*5*), and a value of 3025 cm^{-1} for the antisymmetric CH stretching fundamental, the calculated shifts summarized in Table III for the remaining two possible assignments are readily obtained. The agreement between the calculated and the observed isotopic shifts for the in-plane HCS deformation fundamental is marginal, even considering the likelihood of substantial anharmonic corrections, whereas the agreement for the out-of-plane deformation is excellent. It is concluded that the 993 cm^{-1} absorption can best be assigned to the out-of-plane deformation fundamental of H_2CS.

The 1063 cm^{-1} absorption lies in the region in which the C═S stretching fundamental of H_2CS is to be expected. The C–S stretching absorption of CH_3SH has been assigned at 710 cm^{-1} (*16*), whereas the vibrational fundamental of CS is observed in these experiments at 1276 cm^{-1}. Similarly, the C–O fundamental of CH_3OH lies near 1040 cm^{-1}, the C═O fundamental of H_2CO appears in argon-matrix experiments at 1746 cm^{-1}, and the fundamental absorption of CO is observed at 2140 cm^{-1}. It should be noted that, because of the interaction of hydrogen-atom motions with the carbon–oxygen and carbon–sulfur stretching vibrations, a force constant comparison would have been more satisfactory. However, present data for H_2CS do not suffice for the calculation of an adequate set of force constants. An attempt has been made to estimate the position of the C═S stretching absorption of D_2CS, assuming that the 1063 cm^{-1} peak is contributed by the corresponding absorption of H_2CS. The symmetrized *G* matrix (*17*) was calculated for H_2CS and D_2CS, and the 4 × 4 secular determinant for the a_1 symmetry block was solved to obtain the frequencies for various assumed sets of diagonal force

Table III

Isotopic Shift (cm^{-1}) of 993-cm^{-1} Absorption Compared to that Calculated for Deformation Fundamentals of H_2CS

Species	Obs.	In-Plane HCS Deformation	Out-of-Plane Deformation
$H_2{}^{12}CS$	993.0	(993.0)	(993.0)
$H_2{}^{13}CS$	984.8	987.2	984.0
$HD^{12}CS$	895	.....	893.8
$D_2{}^{12}CS$	783	755.2	782.2

constants. When the CH stretching force constant and the CS stretching force constant were assumed to equal 4.83 and 6.8×10^2 $N \cdot m^{-1}$, respectively, and the CH_2 and HCS deformation force constants were both assumed to equal 0.5×10^{-18} $N \cdot m$, the three totally symmetric fundamentals of H_2CS were calculated to lie at 2929, 1591, and 1047 cm^{-1}, whereas the corresponding fundamentals of D_2CS were calculated to lie at 2146, 1203, and 899 cm^{-1}. (Because of the redundancy of the problem, the fourth frequency equals zero.) Variation of the values of the deformation force constants established that for both molecules the intermediate frequency corresponds to the CH_2 (CD_2) deformation fundamental. Although a value of 1591 cm^{-1} is exceptionally high for a CH_2 deformation fundamental, the arguments of Johns and Olson (*9*) suggest that this fundamental of H_2CS may lie somewhat above 1500 cm^{-1}. If a lower frequency is appropriate for this fundamental, its interaction with the CS stretching fundamental would be expected to be enhanced, and the shift in the CS stretching fundamental on deuteration of the molecule is some 148 cm^{-1} in the present calculation, with relatively little interaction between the CS stretching and the CS_2 deformation motions. Using the slightly higher observed value of 1063 cm^{-1} for the CS stretching fundamental, the shift on deuteration might be expected to be approximately 150 cm^{-1}, placing the CS stretching fundamental of D_2CS near 913 cm^{-1}. In view of the approximations of the calculation and the neglect of anharmonicity, the assignment of the 941 cm^{-1} absorption to the CS stretching fundamental of D_2CS would be reasonable, indeed. Furthermore, the CS stretching fundamental of HDCS would be expected to lie very near 1000 cm^{-1}. As already noted, in the CD_3SH experiments an absorption at 994 cm^{-1} grew in intensity on mercury-arc irradiation of the sample. This absorption was attributed to CD_4, which possesses a prominent absorption at this position and which would also be expected to grow in intensity under these experimental conditions. It is quite conceivable that HDCS also contributes to the 994 cm^{-1} absorption. Thus, all of the data are consistent with the assignment of the 1063 cm^{-1} absorption to the CS stretching fundamental of H_2CS.

Although Johns and Olson (*9*) assigned the 2874 cm^{-1} band to the first overtone of the in-plane CH_2 wagging fundamental, placing this fundamental near 1438 cm^{-1}, their experimental data do not definitively exclude the alternative assignment of this band to the first overtone of the totally symmetric CH_2 deformation fundamental. Therefore, it is necessary also to consider the possible assignment of the 1063 cm^{-1} H_2CS absorption to the in-plane CH_2 wagging fundamental. Using the same procedures as in considering this assignment for the 993 cm^{-1} absorption, the in-plane CD_2 wagging fundamental is readily estimated to lie near 810 cm^{-1}, and the CHD wagging fundamental would be expected to appear near 935 cm^{-1}, the mean of the frequencies of the CH_2 and CD_2 modes. The CD_2 wagging fundamental absorption should be significantly weaker than the corresponding CH_2 or CHD absorptions, and absorptions due to other products at 815 and 819 cm^{-1} in the CD_3SH photolysis experiments may possibly have obscured the D_2CS absorption. However, this is rather unlikely, since the relative intensities of the out-of-plane deformation fundamental absorptions indicate that a higher concentration of D_2CS than of HDCS was present. Therefore, the assignment of the 1063 cm^{-1} absorption as the CS stretching fundamental of H_2CS appears to be preferable.

Unfortunately, the matrix experiments have provided no further information regarding the higher frequency deformation fundamentals. Presumably the fundamental absorption near 1438 cm^{-1} was obscured by the prominent CH_3SH absorption in this spectral region. No evidence was obtained for a higher frequency totally symmetric CH_2 deformation mode. Conceivably this absorption was obscured by the prominent 1530 cm^{-1} CS_2 absorption. However, there was no evidence for the corresponding absorption in the CD_3SH studies, which indicates that any such absorption must be relatively weak. A weak, broad absorption typically appeared at 1753 cm^{-1} in photolyzed Ar:CH_3SH experiments and grew on subsequent mercury-arc irradiation of the sample. However, this absorption had its counterpart at 1737 cm^{-1} in the CD_3SH photolysis studies, which indicates that the vibration responsible for it does not involve a significant hydrogen-atom motion. The assignment of this broad band to H_2CO impurity is also unlikely, since a 40 cm^{-1} shift in the carbonyl absorption of D_2CO has been observed in matrix experiments (*18*).

The proposed vibrational assignment for matrix-isolated H_2CS is compared with that suggested by Johns and Olson (*9*) in Table IV. Taking into account the lack of any direct experimental data on the lower frequency fundamentals in the gas-phase study, the agreement is quite satisfactory.

Photolytic Processes Characteristic of the Matrix Studies

The vacuum-ultraviolet photolysis of CH_3SH in a matrix environment may be compared with the corresponding studies of the closely related CH_3OH molecule (*18*). In the CH_3OH photolysis studies, there was extensive secondary photolysis of the sample, leading to prominent absorptions due to HCO and CO, as well as to absorptions assigned to CH_2OH and to H_2CO. Both CH_2OH and HCO photolyzed on subsequent exposure of the sample to mercury-arc radiation; CH_2OH photodecomposition occurred on exposure of the sample to 2300–2800 Å radiation, whereas HCO photodecomposition occurred because of predissociation of the molecule in the 8600–4600 Å spectral region (*19*). It would thus be predicted that extensive stripping of hydrogen atoms from CH_3SH would occur, leading to the stabilization of a significant concentration of CS, and that, of the intermediate species, H_2CS, like H_2CO, would be likely to be photolytically the most stable.

Table IV

Proposed Vibrational Assignment for H_2CS

Vibration	Symmetry	Description	Frequency (cm^{-1}) Gas Phase[(a)]	Frequency (cm^{-1}) Ar Matrix
ν_1	a_1	Symmetric CH stretch	2971	2970
ν_2	a_1	Symmetric CH_2 bend	>1550	
ν_3	a_1	CS stretch	∿1150	1063
ν_4	b_1	Out-of-plane deformation	∿1100	993
ν_5	b_2	Antisymmetric CH stretch	3025	∿3028
ν_6	b_2	CH_2 wag	1438	1437

(a) Reference (9).

Despite these expected similarities between processes characteristic of the photolysis of CH_3OH and of CH_3SH in a matrix environment, there are important differences between the behaviors of the two systems. Calvert and Pitts (*20*) have summarized spectroscopic and photochemical studies on CH_3SH prior to about 1965. The absorption spectrum of CH_3SH has a maximum near 2400 Å and then climbs steeply beyond about 2150 Å, and at 2537 Å photodecomposition to produce $CH_3S + H$ predominates. More recent studies, summarized by Bridges and White (*21*), are also consistent with the formation of CH_3S. In addition to the photolytic rupture of the sulfhydryl group, the CH_3SH molecule is also subject to photodecomposition into $CH_3 + SH$. In flash photolysis studies in which the radiation was peaked around 1950 Å, Callear and co-workers (*2*, *3*) obtained evidence for a ratio of 1 to 1.7 between C–S and S–H bond scission. Studies of the gas-phase photodecomposition of CH_3SH using both 2537 and 2140 Å radiation have led Bridges and White to conclude that both primary processes are important at both wavelengths. In a later paper, Bridges and White (*22*) reported gas-phase experiments confirming that the reaction of H atoms produced with excess kinetic energy with CH_3SH to produce $CH_4 + SH$ and/or $CH_3 + H_2S$ plays an important role. They concluded that CH_4 results from the reaction of "hot" H atoms but that $H_2 + CH_3S$ can result from the reaction of either thermal or "hot" H atoms with CH_3SH. No experiments on isotopically substituted CH_3SH samples were reported in either the 2140 or the 1950 Å photolysis studies.

In the matrix experiments, the prominence of the absorptions of CS_2 and of CH_4 provides evidence for the importance of C–S bond rupture upon either mercury-arc or vacuum ultraviolet photoysis of the sample. This result may be contrasted with the observations in the methanol photolysis studies, in which there was little evidence for C–O bond rupture. Since H atoms would be expected to lose excess kinetic energy to the argon lattice in the matrix experiments, it seems difficult to rationalize the prominent absorptions of CH_4 in the mercury-arc photolysis experiments on the basis of a "hot" H-atom reaction. However, since diatomic molecules cannot migrate through an argon lattice at 14 K, the primary process in which $CH_3 + SH$ are produced would be expected to be followed by rapid cage recombination. If there is a substantial probability of the formation of $CH_4 + S$ on cage recombination, it would be easy to explain the prominent CS_2 product in the experiments in which CH_3SH was photolyzed by mercury-arc radiation. The photodecomposition of CH_3S may also play a significant role in the observed S-atom production. Very little is known about the spectroscopic or photochemical properties of this species. Rosengren (*23*) has attributed an absorption band near 4000 Å to simple alkylthiyl ($RS^\cdot$) radicals, and Goldberg (*24*) has attributed a band with maximum near 3700 Å to CH_3S resulting from the ultraviolet irradiation of the water clathrate of CH_3SH. Callear and co-workers (*2*, *3*) have presented chemical evidence for the assignment of a diffuse band at 2185 Å to CH_3S. It is relatively unlikely that species such as H_2CS and HCS, with multiply bonded carbon and sulfur, should provide a photolytic source of sulfur atoms.

The most likely source of H_2CS on mercury-arc irradiation of matrix-isolated CH_3SH samples which had previously been subjected to vacuum ultraviolet radiation is the photodetachment of an H atom from CH_3S. Although secondary photolysis processes, necessary for the formation of species such as HCS and CS, also play an important role in the matrix experiments, formation of H_2CS by the $HCS + H$ reaction would be expected to be relatively improbable. The failure to observe significant H_2CS growth on mercury-arc irradiation of the trapped products of the pyrolysis of *s*-trithiane can be understood if little CH_3S is present in this system.

The mechanism by which HDCS is produced in the CH_3SD and CD_3SH photolysis studies is of considerable interest. The photodetachment of the sulfhydryl hydrogen in the primary photolysis process would lead to CH_3S and CD_3S, respectively. In the matrix isolation studies on methanol (*18*), the primary photolysis product was found to be CH_2OH, but this molecule photodecomposed by the rupture of the OH bond, resulting in the stabilization of only a small concentration of HDCO on photolysis of either CH_3OD or CD_3OH. Because the SH bond is generally weaker than the OH bond, CH_2SH would be expected to undergo photodetachment of the sulfhydryl hydrogen, failing to provide a mechanism for the formation of HDCS in the mixed isotopic experiments. It is conceivable that vacuum-ultraviolet irradiation of matrix-isolated CD_3SH samples leads to a CD bond rupture, which may be followed by rearrangement of CD_2SH to a more stable CHD_2S structure. This molecule, in turn, may undergo H-atom photodetachment, leading to the formation of both D_2CS and HDCS. Only a small concentration of HDCS was observed in the study of the mercury-arc photolysis of CH_3SD, consistent with the onset of such a process at relatively high photon energies.

It is likely that such reaction intermediates as CH_3S and HCS contribute to the observed spectrum in the CH_3SH photolysis experiments. However, present data do not suffice for their positive identification.

CONCLUSIONS

Absorptions at 993 and 1063 cm^{-1} in the matrix isolation experiments can be assigned to the out-of-plane deformation and the C=S stretching fundamentals, respectively, of H_2CS. In addition to confirming this assignment, the isotopic data suggest that the photolysis of CH_3SH by radiation of wavelength shorter than about 2500 Å may lead to the rupture of a CH bond, followed by rearrangement of a CH_2SH intermediate to CH_3S.

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REFERENCES

1. A. JONES AND F. P. LOSSING, *J. Phys. Chem.* **71**, 4111 (1967).
2. A. B. CALLEAR, J. CONNOR, AND D. R. DICKSON, *Nature* **221**, 1238 (1969).
3. A. B. CALLEAR AND D. R. DICKSON, *Trans. Faraday Soc.* **66**, 1987 (1970).
4. D. R. JOHNSON AND F. X. POWELL, *Science* **169**, 679 (1970).
5. D. R. JOHNSON, F. X. POWELL, AND W. H. KIRCHHOFF, *J. Mol. Spectrosc.* **39**, 136 (1971).
6. Y. BEERS, G. P. KLEIN, W. H. KIRCHHOFF, AND D. R. JOHNSON, *J. Mol. Spectrosc.* **44**, 553 (1972).
7. M. W. SINCLAIR, N. FOURIKIS, J. C. RIBES, B. J. ROBINSON, R. D. BROWN, AND P. D. GODFREY, *Australian J. Phys.* **26**, 85 (1973).
8. L. H. DOHERTY, J. M. MCLEOD, AND T. OKA, *Astrophys. J.* **192**, L157 (1974).
9. J. W. C. JOHNS AND W. B. OLSON, *J. Mol. Spectrosc.* **39**, 479 (1971).
10. D. E. MILLIGAN AND M. E. JACOX, *J. Chem. Phys.* **47**, 5146 (1967).
11. D. E. MILLIGAN, M. E. JACOX, AND L. ABOUAF-MARGUIN, *J. Chem. Phys.* **46**, 4562 (1967).
12. J. W. HASTIE, R. H. HAUGE, AND J. L. MARGRAVE, *High Temp. Sci.* **1**, 76 (1969).
13. R. MECKE AND H. SPIESECKE, *Chem. Ber.* **89**, 2535 (1956).

14. G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed., p. 523, Van Nostrand, Princeton, N. J., 1950.
15. I. F. Trotter and H. W. Thompson, *J. Chem. Soc.* **1946**, 481.
16. I. W. May and E. L. Pace, *Spectrochim. Acta* **24A**, 1605 (1968).
17. E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," pp. 54–145, McGraw-Hill, New York, 1955.
18. M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.* **47**, 148 (1973).
19. J. W. C. Johns, S. H. Priddle, and D. A. Ramsay, *Discussions Faraday Soc.* **35**, 90 (1963).
20. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," pp. 488–491, Wiley, New York, 1966.
21. L. Bridges and J. M. White, *J. Phys. Chem.* **77**, 295 (1973).
22. L. Bridges and J. M. White, *J. Chem. Phys.* **59**, 2148 (1973).
23. Kj. Rosengren, *Acta Chem. Scand.* **16**, 1418 (1962).
24. P. Goldberg, *J. Chem. Phys.* **40**, 427 (1964).