The generation and vibrational spectrum of matrix isolated thioformaldehyde and dideuterothioformaldehyde

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The photolysis of inert matrix isolated methylene trithiocarbonate at 10 K has been shown to be a clean source of thioformaldehyde. The CH_2S and CD_2S molecules produced this way are indefinitely stable under these conditions and their FTIR spectra could be recorded. A normal coordinate analysis has been carried out and all the normal frequencies of both molecules have been assigned.

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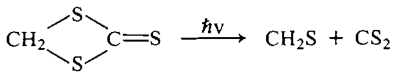
La photolyse de la matrice inerte de trithiocarbonate de méthylène obtenu à 10 K, a montré qu'elle est une source propre de thioformaldéhyde. Les molécules de CH_2S et de CD_2S obtenues de cette façon sont indéfiniment stables dans ces conditions et on peut enregistrer leurs spectres de IR-TF. On a réalisé une analyse normale de coordonnées et on a identifié toutes les fréquences normales de ces deux molécules.

[Traduit par le journal]

Thioformaldehyde **1**, although known in its trimer form for decades (1), has only recently been prepared in its pure monomeric form by the thermolysis of methylsulfenyl chloride in the presence of stoichiometric amounts of hydrogen chloride (2). Several other methods have been described for the generation of **1** (3) but most of them are also based on thermolysis, which poses severe constraints on the use of spectroscopic methods of analysis because of the tendency of **1** to trimerize. Infrared studies have been reported in the gas- and argon-matrix phase but in both cases the method of generation, H-abstraction by fluorine atoms (4) and vacuum uv photolysis of CH_3SH (5), resulted in the formation of substantial amounts of by-products that obscure large parts of the spectrum of **1**, and therefore the results are fragmentary. Recently more detailed studies of the spectrum of **1** by laser stark spectroscopy in the 10 μm region (6), and by single rotational level resonance fluorescence (7), have been reported and in parallel developments a force field and the vibrational spectrum have been calculated for **1** by an *ab initio* mo computation (8).

We have recently reported that photolysis of vinylene trithiocarbonates (9) and thioxocarbonates (10) resulted in the extrusion of CS_2 and COS and the formation of thiirenes and ketenes, respectively. It appears, therefore, that elimination of CS_2, which is reasonably transparent in the 3500–400 cm^{-1} region, is a primary photochemical process of trithiocarbonates and, consequently, methylene trithiocarbonate **2** should be an excellent source compound for the generation of **1**.



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In the present article we wish to report the generation of thioformaldehyde **1** and dideuterothioformaldehyde **3** by the photolysis of argon-matrix isolated methylene trithiocarbonate **2** and dideuteromethylene trithiocarbonate **4** respectively at 10 K. We have also reexamined the ir spectra of **1** and **3** with the aid of FTIR spectroscopy, allowing the assignment of the ir frequencies of **1** and **3**, and have carried out a normal coordinate analysis.

Experimental

An Air-Products and Chemicals Inc. Model CS-202 Displex closed-cycle-helium refrigeration system coupled to a high vacuum line was employed as described before (11). The light source was a Hanovia low pressure resonance mercury lamp equipped with a Vycor filter. Mass spectra were recorded on a Metropolitan Vickers MS-12 spectrometer at an ionization potential of 70 eV and ir spectra of matrix isolated species were obtained on a Nicolet 7199 FT infrared spectrophotometer at 1 cm^{-1} resolution.

Methylene trithiocarbonate **3** was prepared as described (12) and purified by sublimation; mp 55–56°C; ms (30°C): 122(70) 76(44.5) 46(100); and methylene trithiocarbonate-d_2 **4** (99% *d*) was prepared similarly from diiodomethane (99% *d*, Merck, Sharp and Dohme Canada Ltd.); ms (50°C): 124(38.8) 76(46.1) 48(100).

Results and discussion

Photolysis of argon-matrix isolated **2** at 10 K and at $\lambda = 254$ nm resulted in the disappearance of the initial ir spectrum, Fig. 1a, and the appearance of a new spectrum, Fig. 1b, in which CS_2 could be readily identified by the absorptions at 2180(w), 1528(vs), and the $^{13}CS_2$ satellite at 1479(w) cm^{-1}. The remaining absorptions could be clearly identified as thioformaldehyde **1** by the agreement with

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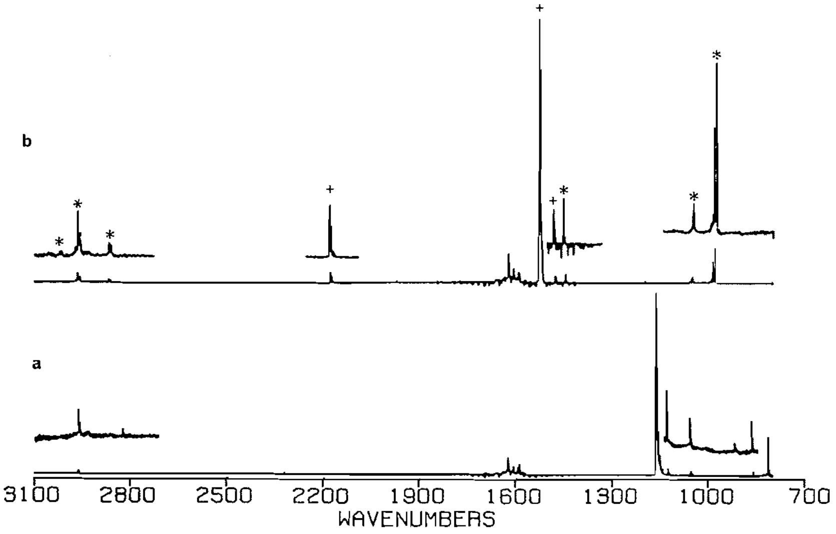

FIG. 1. (*a*) FTIR spectrum of argon-matrix isolated methylene trithiocarbonate **2**. (*b*) After 10 min photolysis at λ = 254 nm radiation. Bands marked (+) are assigned to CS_2 and bands marked (*) are assigned to thioformaldehyde-d_0 **1**.

TABLE 1. Observed frequencies of CH_2S (cm^{-1})

	Frequencies						
	This work[a]	[b]	[c]	[d]	[e]	[f]	Δv[g]
C—H str	3022–3017	3025	3028 sh	—	3024.62	3024.6	−8
	2965–2958	2971	2970–2962	—	2971.03	2971.0	−6
	2869–2864	2870	2874	—			
C═S	1052–1054	—	1056–1063	1059	1059.20	1059.2	−7
CH_2 def	1447	—	—	—	1457.3	1447.0	−10
	982, 980		988–993	990	990.19	990.2	−10.2
	992, 988, 986			991	991.01	991.0	−2

[a] Argon-matrix photolysis; the strongest band in each group is underlined.
[b] Gas-phase, taken from ref. 4.
[c] Argon-matrix, taken from ref. 5.
[d] Gas-phase, laser stark spectroscopy taken from ref. 6.
[e] Gas-phase, single rotational level resonance fluorescence, taken from ref. 7.
[f] Gas-phase FTIR values, taken from ref. 13.
[g] $v_{gas} - v_{matrix}$.

those absorptions that have previously been assigned to **1**, Table 1. All the absorptions appeared as doublets, indicating different trapping sites (14). The photolysis proceeded rapidly and cleanly to completion without the formation of other products, in agreement with the mass spectrum of **2** which showed exclusive decomposition into CS_2 and **1** under electron impact. The split absorptions of argon-matrix isolated **1** have been reported to be replaced by single absorptions in a nitrogen matrix (5). However, in our case, although nitrogen-matrix experiments resulted in single absorptions for CS_2, the splitting of the absorptions for **1** in nitrogen, xenon, or CO matrices remained. In each case only the strongest band, for each fundamental, underlined in Table 1, will be mentioned in the assignments and these have been used in the calculations.

The exclusive formation of CS_2 (CS was not detected), and the good agreement between the remaining spectrum and the known CH_2S absorptions leave no doubt that **1** is responsible for the observed spectrum and that **2** is a clean source compound for the photochemical generation of **1**. Similarly, photolysis of dideuteromethylene trithiocarbonate **4** resulted in the formation of CS_2 and thioformaldehyde-d_2, **3**, Fig. 2, in which a similar matrix effect in the splitting of the CS_2 and **3** bands was observed upon changing the host from argon to nitrogen. The observed bands are listed in Table 2.

Thioformaldehyde has a planar structure with C_{2v} symmetry. The six normal vibrations form the representation $3a_1 + b_1 + 2b_2$ and all are ir active.

C—H stretchings

Three bands have been observed for **1** in the

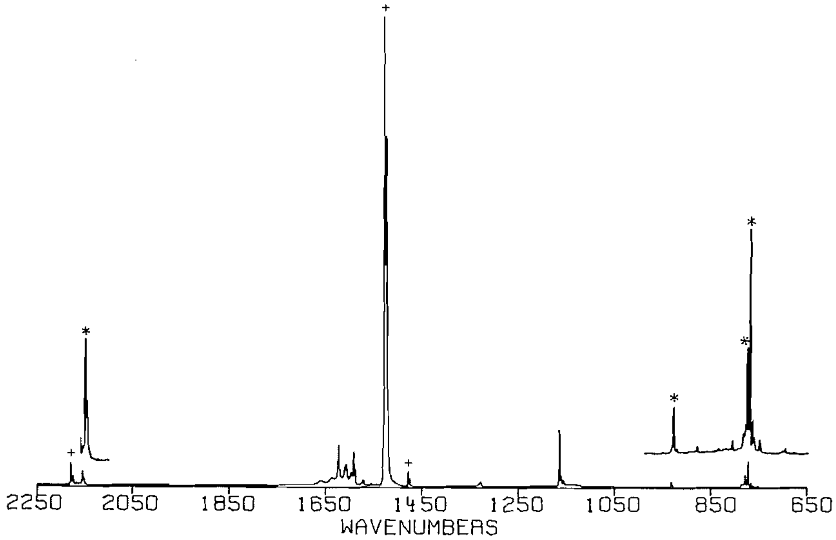

FIG. 2. FTIR spectrum of argon-matrix isolated dideuteromethylene trithiocarbonate **4** after 10 min photolysis with $\lambda = 254$ nm. Bands marked (+) are assigned to CS_2, and bands marked (*) are assigned to thioformaldehyde-d_2 **3**.

C—H stretching region at 2869(w), 2965(m), and 3017(broad, vw) cm^{-1}, in agreement with previous observations, Table 1, whereas in the C—D stretching region **3** featured only a single clear absorption at 2155 cm^{-1}; a weak, very broad absorption centered at 2280 cm^{-1} is also tentatively assigned to **3**. The shift upon deuteration, and the similarity between the relative intensities of the 3017 and 2965 cm^{-1} absorptions of **1** (the antisymmetric C—H stretch is weaker than the symmetric one) and those of formaldehyde (15) support Johns and Olson's assignment of these bands to the antisymmetric and symmetric C—H stretches, respectively (4) based on the rotational assignment of the gas phase spectrum. The 2869 cm^{-1} band originally assigned to a $2\nu_6$ by Johns and Olson (4) should be reassigned to a $2\nu_2$, based on the observed ν_2 (7).

C=S stretch

In agreement with Jacox and Milligan (5) and Bedwell and Duxbury (6) we have retained the assignment of the 1052 cm^{-1} and the 932 cm^{-1} bands to ν(C=S) in **1** and **3**, respectively. The weakness of these bands contrasts with the very strong ν(C=S) at ~1160 cm^{-1}, typical of trithiocarbonates, and also present in the spectra of **2** and **4**.

TABLE 2. Observed frequencies for CD_2S^a (cm^{-1})

	Frequencies			
	This work	From ref. 5	From ref. 13	$\Delta\nu^c$
C—D str	2280 (tentative)	—	—	
	2155, 2152	—	2158.5	−3.5
C=S	932	941	936.2	−4.2
CH_2 def	1167^b	—	1171.8	−4.8
	773	779, 783	781.2	−8.2
	788, 779		757.4	+22.4

^{a}Argon-matrix isolated.
^{b}Only observed in nitrogen-matrix.
$^c\nu_{gas} - \nu_{matrix}$.

C—H deformations

The symmetric CH_2 deformation mode had often been assigned to a band at ~1530 cm^{-1} hidden by the prominent 1528 cm^{-1} CS_2 band, although the actual band had never been seen. Recently, Clouthier *et al.* (7) were able to observe the CH_2 symmetric deformation mode at 1457 cm^{-1}. In argon and xenon matrices the band appears at 1447 cm^{-1}, and the fact that the band could not be seen in the nitrogen-matrix experiments in which there is a shift between +2 and +11 cm^{-1} in the position of all the other bands may be due to the fact that the a_1 CH_2 deformation mode experiences a larger shift of +30 cm^{-1} and becomes hidden in the $^{13}CS_2$ satellite at 1479 cm^{-1}. Similarly, upon deuteration no band is observed in the argon-matrix photolysis that could be assigned to the symmetric CD_2 def, which is probably obscured by the prominent 1165 cm^{-1} absorption of **2**. However, in nitrogen matrices a distinct absorption could be observed at 1167 cm^{-1}, Fig. 3.

For the remaining CH_2 deformations, the out-of-plane and the in-plane, there is only one remaining absorption which is apparently split into various bands in the 992–980 cm^{-1} region, Fig. 4. However, in agreement with the recent results of Bedwell and Duxbury (6), Table 1, and on the basis of the splitting as compared to the other bands and their

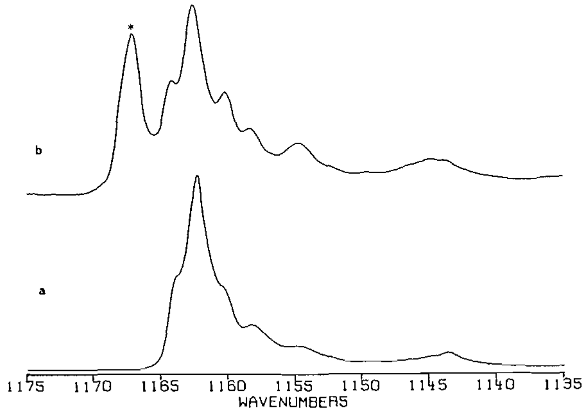

FIG. 3. 1175–1135 cm^{-1} region FTIR spectrum of nitrogen-matrix isolated dideuteromethylene trithiocarbonate (a) after deposition, (b) after 15 min photolysis at λ = 254 radiation (*, assigned to thioformaldehyde-d_2 **3**).

behaviour in different matrices, the presence of two fundamentals is clearly indicated. We have tentatively assigned the strongest to the CH out-of-plane deformation based on the similar situation for formaldehyde (15). These two bands have their counterparts in thioformaldehyde-d_2 at 779 and 773 cm^{-1}.

Product rule

The theoretical Teller–Redlich rule (16) was calculated for thioformaldehyde based on the moments of inertia obtained from the geometrical parameters (R(C═S) = 1.6108 Å, R(C—H) = 1.0925 Å, and α(HCH) = 116.87°) determined by Johnson *et al.* (17) from the microwave spectra. The values obtained are in very good agreement with the observed values for each symmetry species, Table 3, strongly supporting the assignment.

Normal coordinate analysis

The seven internal coordinates used for the calculation are the changes in the three bond lengths (Δr_1, Δr_2, ΔR), the changes in the HCH angle and the two HC═S angles ($\Delta\alpha$, $\Delta\beta_1$, $\Delta\beta_2$) and in the angle between the C═S bond and the HCH plane ($\Delta\beta$). The symmetry coordinates constructed with these internal coordinates are as follows:

$$a_1\quad S_1 = (\Delta r_1 + \Delta r_2)/\sqrt{2}$$
$$S_2 = (2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)/\sqrt{6}$$
$$S_3 = \Delta R$$
$$b_1\quad S_4 = \Delta\delta$$
$$b_2\quad S_5 = (\Delta r_1 - \Delta r_2)/\sqrt{2}$$
$$S_6 = (\Delta\beta_1 - \Delta\beta_2)/\sqrt{2}$$

The force field obtained by Jaquet *et al.* (8) for thioformaldehyde by *ab initio* mo methods was used as our initial force field which was then adjusted to fit the observed frequencies of thioformaldehyde-d_0 **1** and thioformaldehyde-d_2 **3**. The vibrational frequencies were calculated using a computer program (VSEC) written by Schachtschneider (18).

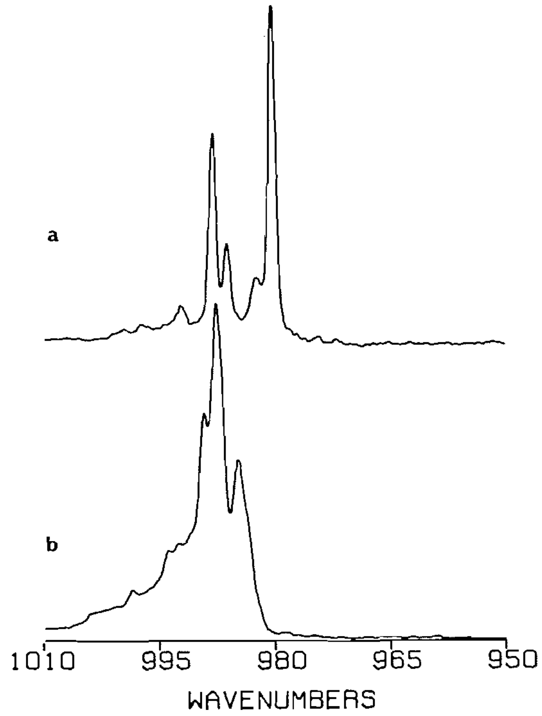

FIG. 4. 1010–950 cm^{-1} region FTIR spectra of methylene trithiocarbonate **2** after λ = 254 nm photolysis for 10 min (a) argon-matrix (b) nitrogen-matrix.

TABLE 3. Theoretical vs. observed product rule ratios[a]

Species	Theoretical	Observed
a_1	0.511	0.519
b_1	0.788	0.789
b_2	0.568	0.586

[a] The observed values are slightly higher due to the anharmonicity. When the band was split, due to matrix effects, only the stronger band was used in the calculation.

The calculated normal frequencies together with the observed values are listed in Table 4. The derived force field, in terms of the symmetry coordinates listed above, is given in Table 5, together with the force field from the *ab initio* calculation (8). The off-diagonal elements which can be calculated fairly reliably by *ab initio* methods have not been changed in the iteration with the exception of F_{56}. The value given by Jacquet *et al.* is rather low, and the one used in our calculations is in agreement with the relationship $F_{13} = 3^{-1/2}F_{56}$

TABLE 4. Observed and calculated frequencies for thioformaldehyde-d_0 and thioformaldehyde-d_2

		Thioformaldehyde-d_0			Thioformadehyde-d_2		
Species		obs.	calcd.	Relative error, %[a]	obs.	calcd.	Relative error, %[a]
a_1	ν_1	2965 (m)	2968	0.1	2155 (m)	2149	0.3
	ν_2	1447 (m)	1450	0.2	1167 (m)	1164	0.3
	ν_3	1052 (w)	1057	0.5	932 (w)	929	0.3
b_1	ν_4	980 (s)	981	0.1	773 (s)	773	—
b_2	ν_5	3017 (vw)	3022	0.2	[2280][b] (vvw)	2243	—
	ν_6	988 (s)	1002	1.4	779 (s)	767	1.5

[a] [ν(calc.) − ν(obs.)]/ν(obs.) × 100.
[b] Tentative, not used for the calculation.

TABLE 5. Derived force field

	Force field	
	This work	From ref. 8[a]
F_{11}	5.021	5.78
F_{12}	0.221	0.22
F_{22}	6.464	7.17
F_{13}	0.140	0.14
F_{23}	−0.261	−0.29
F_{33}	0.454	0.53
F_{44}	0.284	0.32
F_{55}	4.882	5.59
F_{56}	0.240	0.10
F_{66}	0.578	0.62

[a] *ab initio* calculation.

found to be valid in the case of formaldehyde (19). The diagonal force constants are rather different mainly because we could not use anharmonic corrections, but the relative magnitudes agree well with those obtained from the *ab initio* calculation.

After submission of the present manuscript we became aware of a gas-phase FTIR study of thioformaldehyde, **1**, and dideuterothioformaldehyde, **3**, by Mills and co-workers (13). The FTIR gas-phase values have been included in Tables 1 and 2 together with the matrix shift. As seen from the data, the matrix shift is in the range of −3 to −10 cm^{-1} with the exception of ν_6 for CD_2S which has a value of +22 cm^{-1}. When splitting of a band occurs in the matrix, Δν's are computed for the most intense component of the split band.

Acknowledgments

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