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On the Existence of Two Distinguishable Isomers of CS_3: Carbon Trisulfide and Carbon Disulfide *S*-Sulfide[†]

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Abstract: Collision experiments, using tandem mass spectrometry methodologies, provide evidence that carbon trisulfide, CS_3, is a viable molecule in the gas phase, as are its radical cation and anion, respectively. An experimental distinction, whether the species possess D_{3h} or C_{2v} symmetry (**2** versus **3**) could not be achieved, though ab initio MO calculations favor the latter form. Labeling studies point to the existence of a second, hitherto unknown isomer which is assigned as carbon disulfide *S*-sulfide (**6**). This isomer forms a cation radical $\mathbf{6}^{\bullet+}$ whose dissociation pattern is also distinct from that of $\mathbf{2}^{\bullet+}$ ($\mathbf{3}^{\bullet+}$). The experimental findings are supported by ab initio MO calculations.

The continuing interest in the theoretical and experimental characterization of trioxides, XO_3, is due to the particular electronic and structural properties assigned to these species. While there exist several reports on the trioxides of carbon (CO_3),[1] nitrogen (NO_3),[2] and phophorous (PO_3),[3] data on the analogous trisulfides, XS_3, are scarce. Attempts to generate carbon trisulfide (CS_3) by subjecting appropriate precursors to gas-phase pyrolysis failed,[4] and the only indirect support for the existence of a stable CS_3 molecule is provided by a shock wave study of a CS_2/Ar mixture.[5] The complicated kinetics of the reaction in the temperature range 1900–3500 K are interpreted in terms of a disproportionation reaction ($2CS_2 \rightarrow CS_3 + CS$), followed by a rapid bimolecular decay of the CS_3 transient ($CS_3 + M \rightarrow CS_2 + S + M$).[5a] Polymeric $(CS_3)_n$ ($n \simeq 9$) is formed in the oxidation of $SC(SH)_2$ by bromine.[5b] The cation radical $CS_3^{\bullet+}$ is reported to be generated in ion/molecule reactions of CS_2.[5c] Here, we present experimental evidence that in the gas-phase carbon trisulfide, CS_3, does exist as a stable neutral as well as a radical anion and a radical cation, respectively. In addition, results are reported pointing to the existence of a further, hitherto unknown stable CS_3 isomer, e.g., carbon disulfide *S*-sulfide.

Results and Discussion

Electron impact ionization (70 eV) of 4.5-dioxo-2-thioxo-1.3-dithiolan (**1**)[6] in the negative ion mode (NH_3 is used as an electron moderation gas; $p \simeq 10^{-5}$ Torr) gives rise to an abundant signal at m/z 108 which, according to its isotope pattern, corresponds to the elemental composition $CS_3^{\bullet-}$. At a resolution $m/\Delta m \simeq 10^4$ (10% valley definition) the signal at m/z 108 corresponds to a singlet. The mass selection of $CS_3^{\bullet-}$ (m/z 108) using B in a tandem experiment,[7] followed by collisional activation[8] of the 8-keV translational energy beam with helium as collision gas (90% transmission, T), affords the collisional activation (CA) mass spectrum shown in Figure 1. In view of the fact that rearrangement processes in radical anions, compared with radical cations, are of minor importance,[9] we presume that the loss of 2CO from **1** gives rise to the radical anion of carbon trisulfide, the symmetry of which (D_{3h} versus C_{2v}) remains, of course, undecided.

Charge reversal (CR)[10] of mass-selected $CS_3^{\bullet-}$ in a further collision experiment with helium gave rise to the spectrum depicted in Figure 2, which contains a recovery signal for $CS_3^{\bullet+}$ proving that the radical cation $CS_3^{\bullet+}$ as well as its anionic counterpart $CS_3^{\bullet-}$ must reside in a potential well. In addition, the fragment ions observed are, again, compatible with either a C_{2v} or a D_{3h} structure of $CS_3^{\bullet+}$. The fact that the relative intensities of the various products formed upon collision-induced dissociations of $CS_3^{\bullet+}$ and $CS_3^{\bullet+}$ differ very likely reflects the thermochemical stabilities of the various product combinations.

If $CS_3^{\bullet-}$ (m/z 108) is subjected to a neutralization–reionization (NR) experiment,[11] one obtains a clearly detectable recovery signal at m/z 108 (Figure 3); in addition the NR spectrum exhibits a fragmentation pattern which is very close to the one observed in the CR spectrum (Figure 3 viz. Figure 2). Thus, we conclude that in the neutralization experiment, a stable CS_3 molecule has been formed. Due to the vertical nature of the oxidation step $CS_3^{\bullet-} \rightarrow CS_3$ in the collision experiment,[11] we assign for the CS_3 species the as yet unknown carbon trisulfide structure.

A series of further experiments, using a specifically ^{34}S-labeled precursor, were performed aimed at distinguishing between the D_{3h} and C_{2v} forms of CS_3: In the former (**2**) all three sulfur atoms are indistinguishable, whereas the C_{2v} isomer **3** has only two identical sulfur atoms. As a suitable precursor, we have employed

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[†] Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 60th birthday.

[‡] Technische Universität Berlin.

[§] Risø National Laboratory.

(1) Selected references: (a) Pople, J. A.; Seeger, U.; Seeger, R.; Schleyer, P. v. R. *J. Comput. Chem.* **1980**, *1*, 199. (b) van de Duchte, W. J.; Zwart, J. P.; Mulder, J. J. C.; *J. Mol. Struct.* (*THEOCHEM*) **1987**, *152*, 213. (c) McMahon, A. W.; Chowdhury, S.; Harrison, A. G. *Org. Mass Spectrom.* **1989**, *24*, 620.

(2) See, for example: (a) Ishimeta, T.; Fujiwara, I.; Naruge, Y.; Obi, K.; Tanaka, I. *J. Phys. Chem.* **1983**, *87*, 1349. (b) Tshiwaka, T.; Tanaka, I.; Kawaguchi, K.; Hisota, E. *J. Chem. Phys.* **1985**, *82*, 2196. (c) Siegbahn, P. E. M. *J. Comput. Chem.* **1985**, *6*, 182. (d) Kim, B.; Johnston, H. S.; Clabo, D. A.; Jr.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *88*, 3204. (e) Boehm, R. C.; Lohr, L. L. *J. Phys. Chem.* **1989**, *93*, 3430. (f) Davy, R. D.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, 91, 4410.

(3) (a) Henchman, M.; Vigianno, A. A.; Paulson, J. F.; Freedman, A.; Wormhoundt, *J. Am. Chem. Soc.* **1985**, *107*, 1453. (b) Lohr, L. L.; Boehm, R. C. *J. Phys. Chem.* **1987**, *91*, 3203.

(4) (a) O'Connor; B. R.; Jones, F. N. *J. Org. Chem.* **1970**, *35*, 2002. (b) Carlsen, L., Egsgaard, H. Unpublished results. For review, see: (c) Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333. (d) Senning, A. *Tetrahedron* **1986**, *42*, 739.

(5) (a) Arnold, S. J.; Brownlee, W. G.; Kimbell, G. H. *J. Phys. Chem.* **1970**, *74*, 8. (b) Schmidt, M. *Angew. Chem.* **1961**, *73*, 394. (c) Ono, Y.; Linn, S. H.; Prest, H. F.; Gress, M. E.; Ng, C. Y. *J. Chem. Phys.* **1981**, *74*, 1125.

(6) Schönberg, A.; König, B.; Frese, E. *Chem. Ber.* **1965**, *98*, 3303.

(7) (a) *Tandem Mass Spectrometry*; McLafferty, F. W., Ed.; Wiley Interscience: New York, 1983. (b) Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry; Techniques and Applications of Tandem Mass Spectrometry*; VCH Verlagsgesellschaft: Weinheim, 1988.

(8) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

(9) For references see: (a) Budzikiewicz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *93*, 635. (b) Bowie, J. H. *Mass Spectrom. Rev.* **1984**, *3*, 161.

(10) (a) References 8 and 9b. (b) Beynon, J. H. *Proc. Royal Soc.* (*London*) *Ser. A* **1981**, *378*, 1.

(11) For reviews, see: (a) Terlouw, J. K.; Burgers, P. C.; van Baar, B. L. M.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 357. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (c) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (d) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685. (e) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (f) Holmes, J. L. *Mass Spectrom. Rev.* **1989**, *8*, 513. (g) McLafferty, F. W. *Science* In press.

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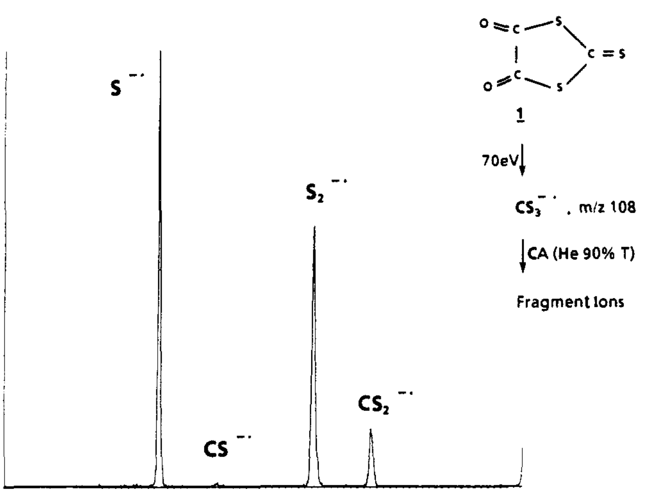


Figure 1. Collisional activation (CA) mass spectrum of $CS_3^{\bullet-}$ (m/z 108).

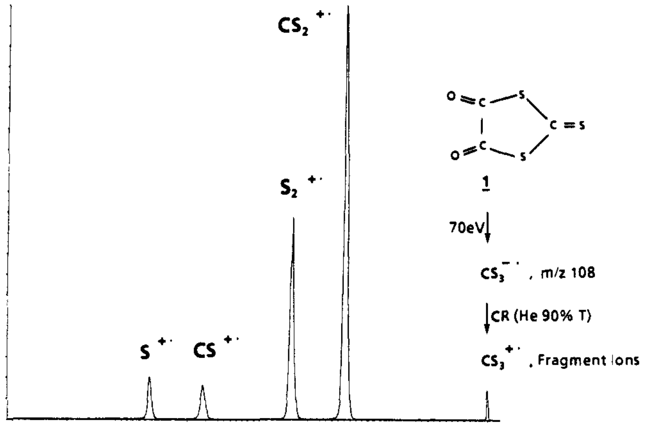


Figure 2. Charge reversal mass spectrum of $CS_3^{\bullet-}$ (m/z 108).

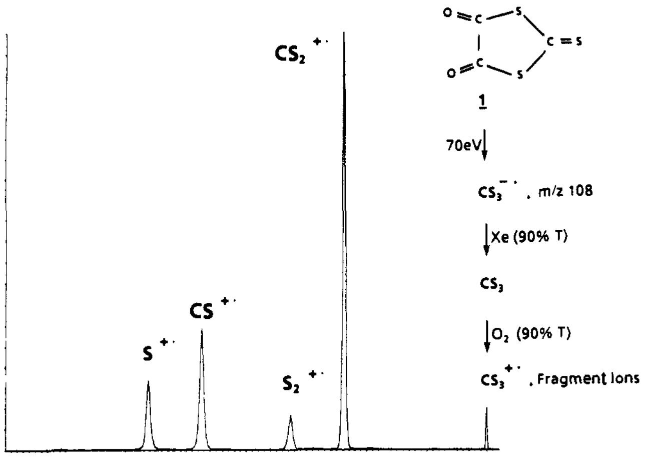


Figure 3. Neutralization-reionization (NR) mass spectrum of $CS_3^{\bullet-}$ (m/z 108).

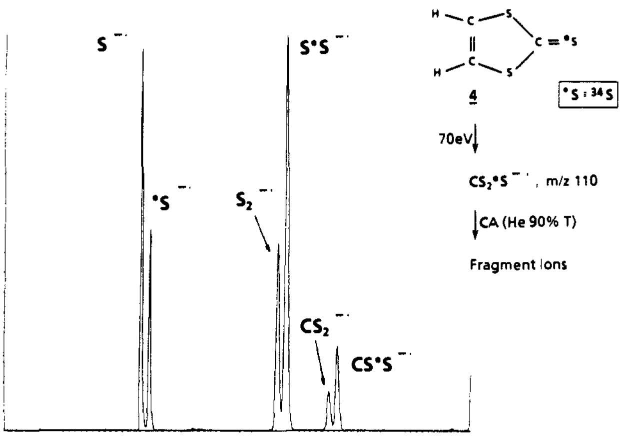


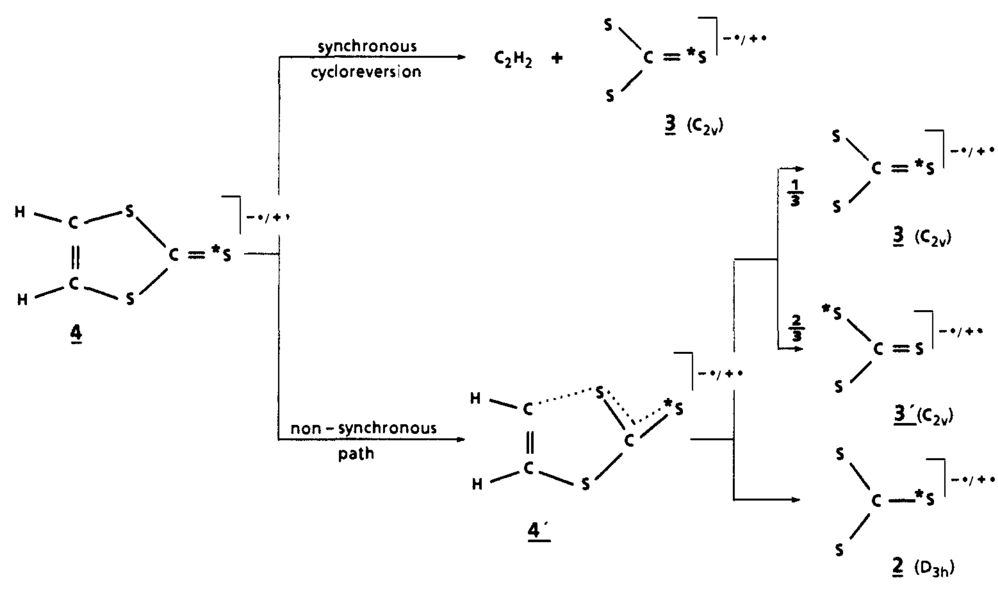
Figure 4. CA mass spectrum of $CS_2{}^{34}S^{\bullet-}$ (m/z 110).

the readily available (see Experimental Section) [^{34}*S*-2-thioxo]-1,3-thiol (**4**).

The CA mass spectrum of $CS_2{}^*S^{\bullet-}$ ($^*S = {}^{34}S$, m/z 110) is given in Figure 4. Comparison of Figure 4 with the analogous spectrum of $CS_3^{\bullet-}$ (Figure 1) clearly reveals the equivalence of all three sulfur atoms of $CS_2{}^*S^{\bullet-}$ with regard to the formations of "$S^{\bullet-}$", "$S_2^{\bullet-}$", and "$CS_2^{\bullet-}$", respectively. No surprise that exactly the same spectrum as in Figure 4 is obtained if the m/z 110 ion of *naturally abundant* ^{34}*S isotopic* $CS_3^{\bullet-}$ ion is subjected to a CA experiment.

A virtually identical result, as far as the $^{32}S/^{34}S$ label distribution is concerned, is obtained if **4** is subjected to dissociative ionization in the positive ion mode (Figure 5). Hence, the so formed, mass-selected $CS_2{}^*S^{\bullet+}$ radical cation, upon collisional activation, gives products which, again, point to a complete equivalence of all three sulfur atoms. The CA mass spectrum of naturally abundant ^{34}S isotopic $CS_3^{\bullet+}$ (not shown) is, again, identical with Figure 5. Expectably, the NR mass spectrum of $CS_2{}^*S^{\bullet+}$ (not shown) also contains the very same pattern of the sulfur isotopes in the various fragment ions.

Scheme I



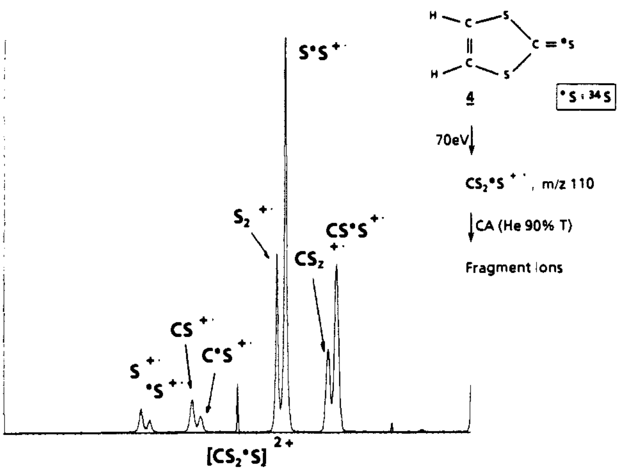


Figure 5. CA spectrum of $CS_2{}^{34}S^{\bullet+}$ from **4** (*m/z* 110).

While one is inclined to interpret these observations as support for the D_{3h} structures **2** for both the radical anion and radical cation of CS_3, a word of caution is indicated. In case that loss of C_2H_2 from **4** is not a synchronous reaction (**4** → **3**) but rather a nonsynchronous reaction (or in the extreme case a process involving an intermediate depicted as **4′** (Scheme I)), the situation is less unambiguous. Dissociation of **4′** to the D_{3h} form **2** can no longer be distinguished from the formation of a statistically weighted mixture of the two C_{2v} forms **3** and **3′**. A further possible complication has to be considered. Even if $CS_3^{\bullet-}$ and $CS_3^{\bullet+}$ are formed as C_{2v} species (molecules, which could also be viewed as ionized dithiirane thiones having a sulfur–sulfur bond), one cannot rule out the possibility that sulfur equilibration is induced in the collision experiment via, for example, an equilibration **3** $\rightleftarrows$ **2** preceding the collision-induced formation of the fragment ions shown in Figures 4 and 5.

As will be shown below, ab initio MO calculations suggest that for both $CS_3^{\bullet+}$ and $CS_3^{\bullet-}$ the C_{2v} form **3** is energetically favored over the D_{3h} isomer **2**.

While the ^{34}S-labeling experiment did not permit a clear-cut distinction of the symmetry of $CS_3^{\bullet+}$, $CS_3^{\bullet-}$, and CS_3, respectively, the investigation of the mono- and doubly-^{34}S-labeled isotopomers **5a** and **5b** of 3-thioxo-1,2-dithiol (**5**) provided evidence that in addition to carbon trisulfide a second stable isomer must exist in the gas phase for the cation radical. For the neutral form of this second isomer the evidence is only circumstantial. Sensitivity problems precluded the study of radical anions generated from **5a** and **5b**.

Electron impact ionization (70 eV) of **5** in the positive ion mode gives a signal for $CS_3^{\bullet+}$. The CA mass spectra of the respective mono- and doubly-^{34}S-labeled cation radicals generated from **5a** and **5b**, are given in Figure 6 (parts a and b). There is no doubt that the isotope distributions in the fragment ions "$CS_2^{\bullet+}$", "$S_2^{\bullet+}$" and "$CS^{\bullet+}$" deviates significantly from the 1:2 distributions typical for a species having three equivalent sulfur atoms. Note, that the CA mass spectrum of naturally abundant ^{34}S-labeled $CS_3^{\bullet+}$ ion (*m/z* 110) generated from **5** shows the expected statistical isotope distribution in the S-containing fragments. A closer inspection of the CA spectra (Figure 6 (parts a and b)) reveals that the spectra can be explained in terms of a binary mixture of two structurally distinct $CS_3^{\bullet+}$ species; one is characterized by having a set of three "equivalent" S atoms, similar to the situation discussed above for the $CS_3^{\bullet+}$ product generated from **1** and **4**. The second isomer is very likely to correspond to the as yet unknown cation radical of carbon disulfide *S*-sulfide ($SCSS^{\bullet+}$). This proposal is evidenced by the following observations: Although the fragmentation patterns of the two "CS_3" isomers display only minor quantitative difference in terms of relative abundancies of the fragment ions formed, the CA spectrum of $CS_2{}^{*}S^{\bullet+}$ (formed from **5a**, Figure 6a) reveals signals due to loss of neutral S, C*S, and S_2 which are *more* intense than expected on the basis of a statistical distribution of $^{32}S_2/^{34}S$. The contribution of this isomer is indicated by the shaded area as well as the bars given in the figures. A virtually complementary situation prevails in the CA spectrum of the $CS{}^{*}S_2^{\bullet+}$ species generated from **5b** (Figure 6b). This second isomer which we assign to have structure $\mathbf{6}^{\bullet+}$ may contribute up to 30% of the CA mass spectra. It remains open whether the 70% of "S-scrambled" species are due to a collision-induced isomerization $\mathbf{6}^{\bullet+} \rightarrow \mathbf{2}^{\bullet+}/\mathbf{3}^{\bullet+}$ of initially formed $\mathbf{6}^{\bullet+}$ or whether $\mathbf{2}^{\bullet+}/\mathbf{3}^{\bullet+}$ are directly generated from **5**.

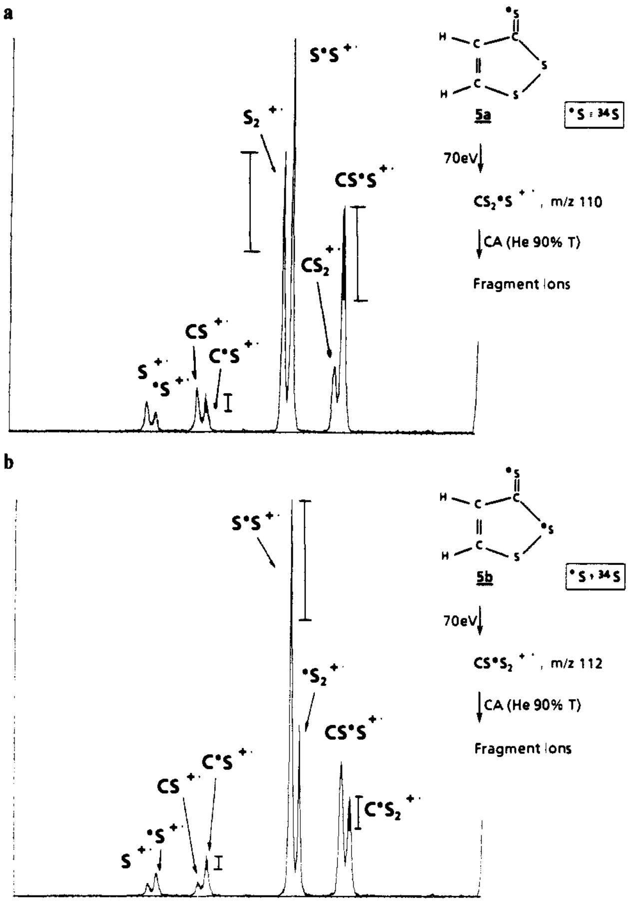


Figure 6. (a) CA mass spectrum of $CS_2{}^{34}S^{\bullet+}$ from **5a** (*m/z* 110) and (b) CA mass spectrum of $CS^{34}S_2^{\bullet+}$ from **5b** (*m/z* 112).

Preliminary ab initio MO calculations (HF/6-31G* + ZPVE) using the CRAY-XMP version of the GAUSSIAN 82 and 86 series of programs[12] support our interpretations that the potential surface of $(CS_3)^{\bullet+}$ must contain at least two minima.[13] At this level of theory $\mathbf{6}^{\bullet+}$ is 14.2 kcal/mol more stable than $\mathbf{3}^{\bullet+}$. Although the D_{3h} form $\mathbf{2}^{\bullet+}$ is also found to correspond to a local minimum (5.7 kcal/mol less stable than $\mathbf{6}^{\bullet+}$), the high-spin contamination calculated for $\mathbf{2}^{\bullet+}$ ($\langle S^2\rangle = 1.76$ compared with 0.89 and 0.78 for $\mathbf{6}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$) casts some doubt on the validity and appropriateness of the level used to characterize the D_{3h} structure. This situation was also noted in the ab initio studies on D_{3h} structures of XO_3 (X = C, N, P).[1a,b,2c–e,3b]

The structural distinction of $\mathbf{6}^{\bullet+}$ versus $\mathbf{2}^{\bullet+}/\mathbf{3}^{\bullet+}$ remains preserved when the $CS_3^{\bullet+}$ cation radical formed from **5a** and **5b** are reduced to neutral CS_3 species in a NR experiment. This follows immediately from the NR mass spectrum of $CS_2{}^{*}S^{\bullet+}$ and $CS{}^{*}S_2^{\bullet+}$ given in Figure 7 (parts a and b). We not only note a clearly detectable recovery signal but also, more importantly, the deviation from the statistical isotope distributions in the fragment ions discussed above is, again, well-reflected in the NR mass spectra. Thus, we tentatively suggest that neutral carbon trisulfide also exists as at least two distinguishable isomers. One corresponds to the D_{3h} (or more likely[15] C_{2v}) form **2** (**3**); the second one is best

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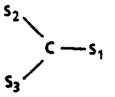
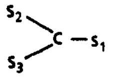
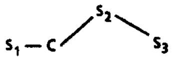
[12] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon University: Pittsburgh, PA, 1984.

[13] Attempts to locate precisely transition states connecting the various neutral and ionic isomers of CS_3 have not yet been successful.

Table I. HF/6-31G* Calculated Total Energies (in hartrees), Zero Point Vibrational Energies (in hartrees), Expectation Values $\langle \hat{S}^2 \rangle$, and Geometries (Bond Length in Å, Bond Angles in deg) of (C,S$_3$) Isomers **2** (D_{3h}), **3** (C_{2v}), and **6** (C_s) and Their Respective Radical Anions and Radical Cations[a,b]


2 (D$_{3h}$)


3 (C$_{2v}$)


6 (C$_s$)

species	E_{total}	ZPVE	$\langle \hat{S}^2 \rangle$	C–S$_1$	C–S$_2$	S$_2$–S$_3$	S$_1$–C–S$_2$	C–S$_2$–S$_3$
3 (triplet)	−1230.338 39	0.007 97	2.03	1.635	1.736		120	
3 (singlet)	−1230.336 45	0.008 81		1.588	1.730		142	
6 (triplet)	−1230.322 34	0.007 41	2.04	1.564	1.714	2.013	137	104
6 (singlet)	−1230.310 90	0.008 19		1.514	1.598	2.092	180	105
$\mathbf{3}^{\bullet -}$	−1230.423 12	0.009 22	0.77	1.662	1.715		128	
$\mathbf{6}^{\bullet -}$	−1230.391 12	0.007 20	0.78	1.613	1.654	2.078	141	110
$\mathbf{2}^{\bullet +}$	−1230.048 59	0.007 69	1.76	1.702			120	
$\mathbf{3}^{\bullet +}$	−1230.035 42	0.008 19	0.78	1.631	1.694		141	
$\mathbf{6}^{\bullet +}$	−1230.057 97	0.008 00	0.89	1.485	1.672	2.036	180	102

[a] For **2** and $\mathbf{2}^{\bullet -}$ the D_{3h} forms do not correspond to local minima. [b] Atom assignment is as indicated in the structures **2**, **3**, and **6** (respectively).

described as a carbon disulfide *S*-sulfide **6**.[14]

Our interpretation of the experimental results is also supported by the ab initio MO calculations. At the 6-31G* + ZPVE level of theory we locate minima for **6** and **3** (but not **2**). For the singlet CS$_3$ species, the C_{2v} isomer **3** is 15.7 kcal/mol *more* stable than carbon disulfide *S*-sulfide (**6**). At the triplet surface, this gap in relative energies is reduced to 9.8 kcal/mol again favoring **3**. As was observed for many other carbon–sulfur compounds,[16] the triplet forms of CS$_3$ are more stable than their singlet isomers.

For the sake of completeness it should be mentioned that 6-31G* calculations (including ZPVE) were also performed for the $(CS_3)^{\bullet -}$ surface. The global minimum corresponds to the C_{2v} species $\mathbf{3}^{\bullet -}$ which is found to be 18.9 kcal/mol more stable than $\mathbf{6}^{\bullet -}$. As stated above, sensitivity problems prevented us from an experimental verification of the latter prediction. Calculated geometries for the various $(CS_3)^{0/\bullet +/\bullet -}$ species are given in Table I together with the relevant total energies.

In summary, it can be concluded that carbon trisulfide, CS$_3$, appears to be a viable molecule in the dilute gas phase, as are its corresponding radical cations and anions. For its isomeric form, SCSS, the experimental data establishes the existence of a stable radical cation SCSS$^{\bullet +}$. For the neutral form **6** the evidence is, for the time being, only circumstantial.

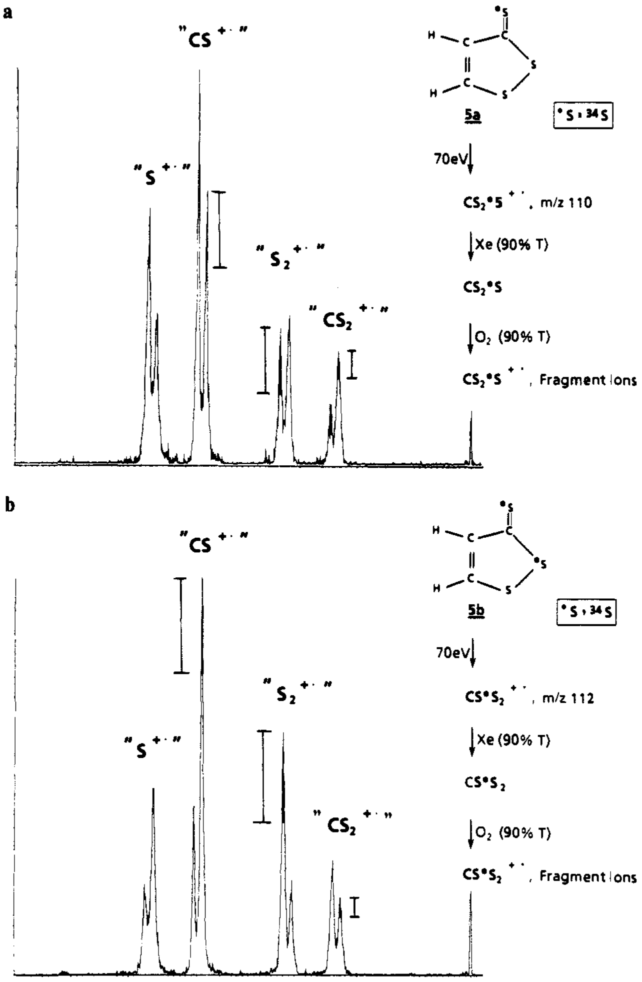


Figure 7. (a) NR mass spectrum of CS$_2{}^{34}$S$^{\bullet +}$ from **5a** (*m/z* 110) and NR mass spectrum of CS^{34}S$_2{}^{\bullet +}$ from **5b** (*m/z* 112).

Experimental Section

The ^{34}*S*-thioxo-1,3-dithiol (**4**) was prepared from 2-seleno-1,3-dithiol (**7**) by direct displacement of selenium with sulfur. **7** (200 mg) was heated (120 °C) with 200 mg of ^{34}S$_8$ (obtained from Monsanto Research Corporation, Miamisburg, OH) for 72 h in an evacuated glass ampoule. The sample was used for mass spectrometric analyses without further purification.

The ^{34}*S*-thioxo-1,2-dithioles (**5a**, **5b**) were prepared by an exchange reaction with **5** as starting material. Heating 200 mg of **5** with 200 mg of ^{34}S$_8$ for 24 h/90 °C lead predominantly to **5a**, whereas heating for 24 h/120 °C lead to an approximate 1:1 mixture of **5a** and **5b**. The samples

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(14) A referee has rightly argued that the "evidence" for a stable neutral species SCSS **6** is not fully convincing as the isotope distribution reported in Figure 7a, b can also be explained if **6** is unstable with respect to dissociation. This follows from the fact that in the NR experiment also the *dissociation products* of neutral **6** will be reionized and recorded as well. A straightforward experiment would be to mass-select *reionized* **6** and subject it to a CA experiment. While this experiment could indeed be performed in other cases[11d,g] using our ZAB-HF-3F machine (BEB configuration), in the present case sensitivity problems prevented a successful experiment. We have also performed exploratory MO calculations for the two most important dissociations of both the singlet and triplet electromers of **6**. The following results were obtained: At RHF/6-31G* + ZPVE, dissociation of **6** (singlet) to CS$_2$/S is endothermic by 20.0 kcal/mol; the generation of CS/S$_2$ costs 24.9 kcal/mol. Thus, the singlet of **6** is stable toward dissociation. However, this is not the case for the thermochemically more stable triplet of **6**. At HF/6-31G* + ZPVE this species *is higher* in energy than its dissociative products CS$_2$/^{3}S (by 23.7 kcal/mol) and CS/^{3}S$_2$ (by 19.1 kcal/mol). As we have not yet succeeded in locating a real transition state for the dissociations of **6**, it remains open to future, more elaborate MO studies to settle this point.

(15) Extended Hückel calculations indicate the D_{3h} form of CS$_3$ (**2**) not to be a minimum. Rather, the postulated equilibration of the sulfur atoms is brought about by valence tautomerism of the C_{2v} form **3**: Calzaferri, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. II* **1975**, 559.

(16) Selected examples include the following. (a) C$_2$S$_2$: Raine, G. P. Schaefer, H. F.; III, Haddon, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 194. Sülzle, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1337. (b) C$_2$SO: Sülzle, D.; Terlouw, J. K.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 628. (c) C$_2$S: Sülzle, D.; Schwarz, H. *Chem. Ber.* **1989**, *122*, 1803.

were used for the mass spectrometric analyses without further purification. The introduction of the second label in **5b** apparently has to be explained by the intermediacy of an S,S biradical.[17]

All mass spectrometric experiments were carried out in a commercially available VG Instruments ZAB-2F mass spectrometer which is of BE configuration (B stands for magnetic and E for electric sector), with standard tandem mass spectrometry conditions (see text).

Acknowledgment. We gratefully appreciate the support of our work by the Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, Graduiertenkolleg Chemie, and the Gesellschaft von Freunden der Technischen Universität Berlin.

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(17) Egsgaard, H.; Carlsen, L. Unpublished results.

Calculation of Excited-State Geometries via the Time-Dependent Theory of Resonance Raman Spectroscopy: Application to the Complexes $Cs_4[W_2OCl_{10}]$ and $Cs_3[Re_2OCl_{10}]$

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Abstract: The calculation of both the excitation profiles of the resonance-enhanced Raman bands and the intensities of the overtone and combination bands of the rich resonance Raman spectra of $Cs_3[Re_2OCl_{10}]$ and $Cs_4[W_2OCl_{10}]$ is reported. The calculation uses the time-dependent theory of Lee, Tannor, and Heller. The geometric changes attendant upon excitation of each molecule from the ground to the excited state in resonance are calculated. All of the excitation profiles and the resonance Raman spectra can be fitted by use of one multidimensional potential surface.

The geometrical changes that a molecule undergoes when it is electronically excited are important in determining its spectroscopic and photochemical properties. Transition-metal complexes are of particular interest because they frequently undergo large displacements along many normal modes when excited. The magnitudes of the displacements can be calculated from the intensities of vibronic bands in electronic emission or absorption spectra if band structure can be observed.[2-6] More commonly, however, only broad unstructured bands are obtained from big transition-metal complexes in condensed media. An alternative method of calculating the displacements uses the intensities in resonance Raman spectra.[7-13] This method is especially powerful for large inorganic molecules in condensed media because most of the displaced modes can be individually observed and calculated even when only a broad envelope is observed in the electronic spectrum. The new time-dependent theory developed by Lee, Tannor, and Heller is especially efficient.[14-17]

The high polarizability of the axial π-bond system of $[M_2OX_{10}]^{n-}$ ions (M = Ru, Re, Os, or W; X = Cl or (in some cases) Br) is well-known to make them ideal species for Raman studies.[18-20] The $[Ru_2OCl_{10}]^{4-}$ ion was established from early crystallographic work to be linear, with D_{4h} symmetry,[21] and many other such ions are known to have this structure.[19] Raman studies using excitation lines at resonance with the lowest allowed electronic transition of the $[Re_2OCl_{10}]^{3-}$ ion (the $e_u^* \leftarrow e_g$, ${}^4E_g \leftarrow {}^4E_u$ transition of the linear Re–O–Re π-bonded system[19]) gives rise to long (up to 12-membered) overtone progressions in the $\nu_1(a_{1g})$, ν_s(ReORe), symmetric Re–O–Re stretching fundamental at 230 cm^{-1}. At least eight progressions in ν_1 are observed in the resonance Raman spectrum of this ion; in most cases, the enabling modes for the $\nu_n + \nu_1\nu_1$ progressions are other Raman-active fundamentals but, in three cases, they are the first and third overtones of infrared-active (Raman inactive) fundamentals. The other isostructural ions give rise to similar resonance Raman spectra.[18-20] The observation of long progressions in a totally symmetric mode offers the opportunity of calculating the geometric changes attendant upon excitation from the ground to the resonant excited state.

In this paper, the geometric changes in the $[W_2OCl_{10}]^{4-}$ and $[Re_2OCl_{10}]^{3-}$ ions upon excitation within the contour of the band assigned to the $e_u^* \leftarrow e_g$ transition are calculated. Excitation profiles of fundamentals, overtone, and combination bands are

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(2) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951 and references therein.

(3) Zink, J. I. *Coord. Chem. Rev.* **1985**, *64*, 93.

(4) Zink, J. I.; Tutt, L.; Yang, Y.-Y. *Am. Chem. Soc. Sym. Ser.* **1986**, *307*, 39.

(5) Preston, D. M.; Shin, K. S.; Hollingsworth, G.; Zink, J. I. *J. Mol. Struct.* **1988**, *173*, 185.

(6) Larson, L. J.; Zink, J. I. *Inorg. Chem.* **1989**, *28*, 3519.

(7) Clark, R. J. H.; Dines, T. J.; Doherty, J. M. *Inorg. Chem.* **1985**, *24*, 2088.

(8) Clark, R. J. H.; Dines, T. J.; Wolf, M. L. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 679.

(9) Clark, R. J. H.; Dines, T. J.; Proud, G. P. *J. Chem. Soc., Dalton Trans.* **1983**, 2019.

(10) Clark, R. J. H.; Dines, T. J.; Kurmoo, M. *Inorg. Chem.* **1983**, *22*, 2766.

(11) Tutt, L.; Tannor, D.; Schindler, J.; Heller, E. J.; Zink, J. I. *J. Phys. Chem.* **1983**, *87*, 3017.

(12) Shin, K. S.; Clark, R. J. H.; Zink, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 4244.

(13) Shin, K. S. K.; Zink, J. I. *Inorg. Chem.* **1989**, *28*, 4358.

(14) Lee, S.-Y.; Heller, E. J. *J. Chem. Phys.* **1979**, *71*, 4777.

(15) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

(16) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822.

(17) Tannor, D.; Heller, E. J. *J. Phys. Chem.* **1982**, *77*, 202.

(18) Clark, R. J. H.; Franks, M. L.; Turtle, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 2473.

(19) Campbell, J. R.; Clark, R. J. H. *Mol. Phys.* **1978**, *36*, 1133.

(20) Campbell, J. R.; Clark, R. J. H. *J. Chem. Soc., Faraday Trans. II* **1980**, *76*, 1103.

(21) Mathieson, A. M.; Mellor, D. P.; Stephenson, N. C. *Acta Crystallogr.* **1952**, *5*, 185.

0002-7863/90/1512-3754$02.50/0