

Kurzmitteilung/Short Communication

CCS and S(C₄)S: The Laboratory Generation of Interstellar Molecules and Their Radical Cations

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The title compounds are generated and characterized in the gas phase by mass spectrometric methods (neutralization-reionization mass spectrometry), and for dicarbon sulfide the experimental results are supported by ab initio MO calculations (HF/6-31G*).

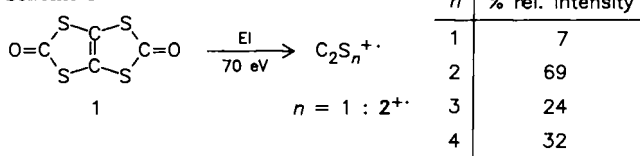
The considerable recent interest¹⁾ in linear and/or quasilinear molecules of the general structure X(C_n)Y (X, Y: lone electron pair, H₂, O, S; n > 2) containing polycumulated double bonds, is partly due to the remarkable spectroscopic and chemical properties of these species, some of which are believed to play a crucial role in the genesis of interstellar molecules.

Unfortunately, in the condensed phases quite a few of these species cannot even be produced as a transient due to their high intermolecular reactivity. This "instability", however, does not reflect an intrinsic property since under appropriate conditions, e.g. in the diluted gas phase, several of these cumulenes could easily be generated. For sulfur-containing cumulenes, representative examples are S=C=C=S²⁾ and S=C=C=O³⁾, which became accessible from the corresponding cation radicals by using the powerful method of neutralization-reionization mass spectrometry (NRMS)⁴⁾.

Here we report on the successful gas-phase generation and characterization of both the cation radical and neutral dicarbon sulfides CCS⁺⁺ (2⁺⁺) and CCS (2), respectively, by using NRMS. The triplet of 2 (³Σ) was recently detected⁵⁾ in interstellar clouds (Taurus Mol. Cloud-1, Sagittari B2, IRC + 10216), and the assignment of the lines was supported by a microwave study of a mixture of species generated by a d.c. glow discharge in a mixture of CS₂ and He^{5b)}. In addition, experimental evidence will be presented which demonstrates that the neutral as well as the cation radical of butatrienedithione **6** and **6**⁺⁺ exist as stable molecules in the gas phase.

Electron impact ionization (70 eV)⁶⁾ of 1,3,4,6-tetrathiapentalene-2,5-dione⁷⁾ (**1**) affords as most important fragments C₂S_n⁺⁺ (Scheme 1), including the interesting C₂S⁺⁺.

Scheme 1



The mass selection of C₂S⁺⁺ (m/z = 56) using B(1)/E in a tandem experiment⁸⁾, followed by collisional activation⁹⁾ of the 8-keV trans-

lational energy beam with helium as collision gas (90% transmission, T), affords the collisional activation (CA) mass spectrum shown in Figure 1. This spectrum, which contains the structure-indicative fragments of CS⁺⁺, S⁺⁺, C₂⁺⁺ and C⁺⁺, is only compatible with a connectivity CCS⁺⁺ (2⁺⁺) and not, for example, C-S-C⁺⁺. In addition, existing thermochemical data¹⁰⁾ for the various product combinations, i.e. CS⁺⁺/C, S⁺⁺/C₂, C₂⁺⁺/S and C⁺⁺/CS support the observed fragmentation pattern intensity in that the production of CS⁺⁺/C corresponds to the energetically most favoured decomposition path.

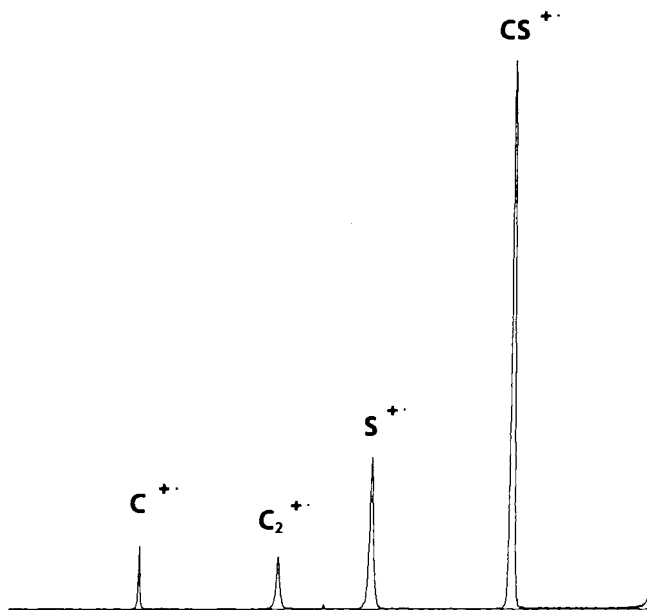


Figure 1. Collisional activation mass spectrum of C₂S⁺⁺ (m/z = 56); collision gas helium (90% T)

If CCS⁺⁺ (2⁺⁺) is subjected to an NRMS experiment, one obtains not only a very abundant recovery signal at m/z = 56 (Figure 2); moreover, the fragmentation pattern is virtually the same as observed in the CA mass spectrum. Thus, we conclude that in the neutralization experiment a stable C₂S species has been formed, which, due to the vertical nature of the electron transfer in the collision experiment⁴⁾, we assign to dicarbon sulfide **2**.

The experimental findings are supported by ab initio HF/6-31G* calculations¹¹⁾ (Table 1). We note the following: (i) The triplet state (³Σ) of **2** is by 31.6 kcal/mol more stable than its singlet electromer

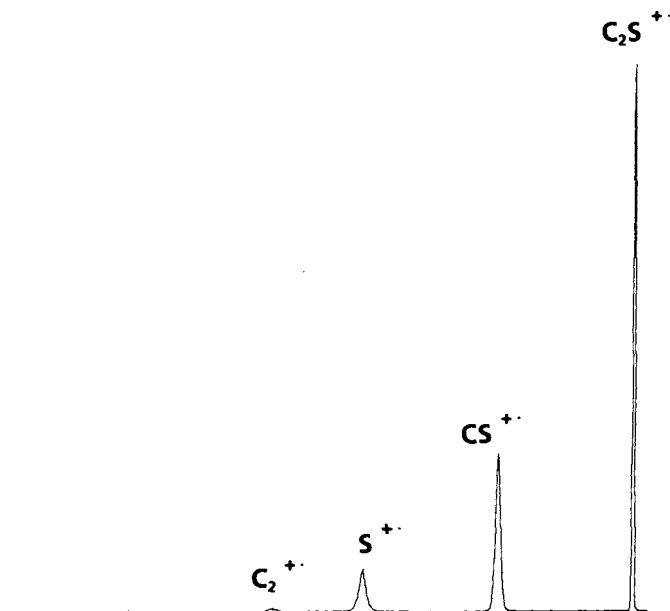


Figure 2. Neutralization-reionization mass spectrum of $C_2S^{+\bullet}$ ($m/z = 56$); xenon 90% T/oxygen 90% T

($^1\Sigma$). This ordering of stabilities of triplet vs. singlet states was also found for $S=C=C=S$ and $S=C=C=O$ ^{1b,2,3}. The adiabatic ionization energy of 32 corresponds to 9.7 eV. (ii) The geometry changes, when comparing the cation radical $CCS^{+\bullet}$ ($2^{+\bullet}$) with its neutral analogues (i.e. 32 and 12), are quite small with a lengthening of the C–C and shortening of the C–S bonds of $2^{+\bullet}$ compared with the neutral molecules. This relatively minor geometry changes may account for the abundant flux of the recovery signal at $m/z = 56$ in the NR spectrum of $C_2S^{+\bullet}$. (iii) Species with a connectivity C–S–C $^{+\bullet}$, or the C_s -symmetric form of $CCS^{+\bullet}$ were not found to correspond to minima. Similarly, a cyclic CCS species is not needed to be taken into consideration. According to the Walsh rules¹², for species containing 14 valence electrons (like C_2S) a linear connectivity is favoured for the ground state.

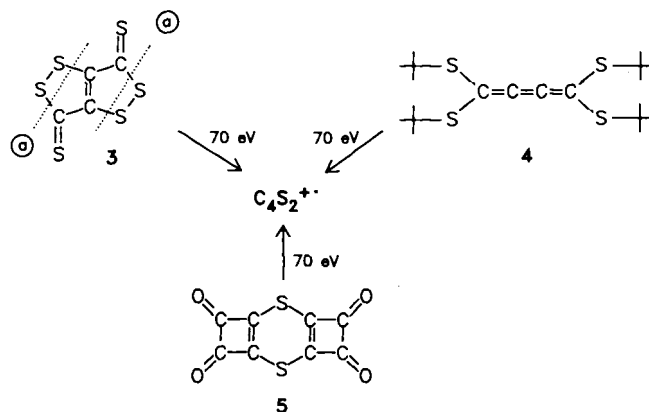
Table 1. Calculated (HF/6-31 G*) geometric and energetic data of C_2S and $C_2S^{+\bullet}$

Species	Total Energy	ZPVE [Hartree]	E_{rel} [kcal/mol]	$\langle \hat{S}^2 \rangle$
$C \overset{1.304}{\text{---}} C \overset{1.549}{\text{---}} S$ 32 ($^3\Sigma$)	-473.103042	0.007262	0	2.10
$C \overset{1.306}{\text{---}} C \overset{1.554}{\text{---}} S$ 12 ($^1\Sigma$)	-473.053488	0.008134	31.6	–
$C \overset{1.379}{\text{---}} C \overset{1.512}{\text{---}} S$ $2^{+\bullet}$ ($^3\Sigma$)	-472.746611	0.006171	222.9	1.09

As mentioned in the introductory part, cumulenes are of particular interest. This holds true in particular for cumulenes having an even carbon number as these molecules, in comparison with their odd-numbered analogues, are believed to be significantly less stable^{1b,13}. In fact, there is no experimental report on the successful generation and characterization of $S=(C_n)=S$ ($n = 4, 6$, etc.). Here, we will present evidence that butatrienedithione ($n = 4$) is accessible in the gas phase.

Electron impact ionization (70 eV) of 1,2-dithiolo[4,3-*c*]-[1,2]dithiol-3,6-dithione¹⁴ (**3**) gives rise to an intense signal at $m/z = 112$, which, according to its isotope pattern and to exact mass measurements, has the elemental composition $C_4S_2^{+\bullet}$. The same fragment is also abundantly generated from tetrakis(*tert*-butylthio)butatriene¹⁵ (**4**) and from dicyclobuta[*b,e*][1,4]dithiine-1,2,4,5-tetraone¹⁶ (**5**).

Scheme 2



The mass selection of $C_4S_2^{+\bullet}$ ($m/z = 112$) using B(1)/E, followed by CA (collision gas: helium, 80% T), gives rise to the CA mass spectrum shown in Figure 3. This spectrum is identical for all three precursors **3**, **4**, and **5**. Apart from minor signals at $m/z = 100, 88, 76$, and 64 , which are due to loss of C_x ($x = 1-4$), the CA mass spectrum of $C_4S_2^{+\bullet}$ (Figure 3) is compatible with a connectivity $S=C=C=C=C=S^{+\bullet}$ ($6^{+\bullet}$), whose genesis from **3** may proceed by the bond ruptures indicated with \textcircled{a} in Scheme 2. Starting from ionized **5**, quite substantial skeletal rearrangement must precede and/or accompany the loss of 4CO to eventually generate a $C_4S_2^{+\bullet}$ species being identical with the one generated from ionized **1** and **2**. The alternative that $C_4S_2^{+\bullet}$, formed from $5^{+\bullet}$, will not

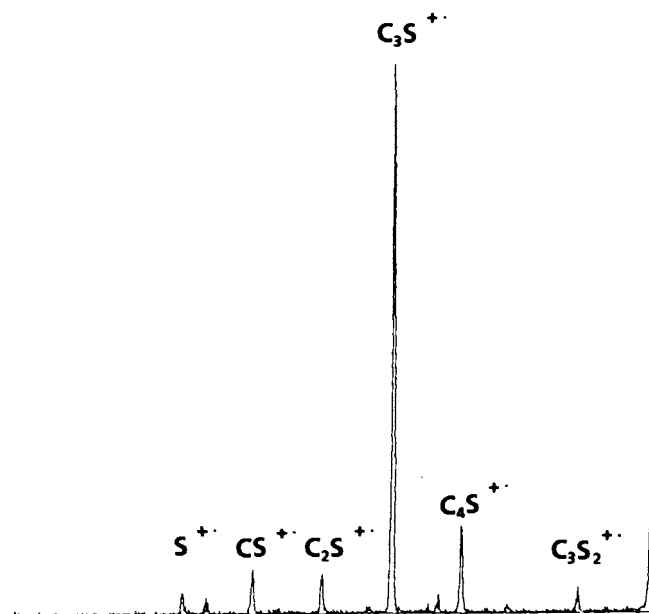


Figure 3. Collisional activation mass spectrum of $C_4S^{+\bullet}$ ($m/z = 112$) generated from **1** $^{+\bullet}$

correspond to 6^{++} but rather (for example a cyclic species having C_2 units) is not supported by its collision-induced dissociations; in particular, it would be difficult to explain the two most abundant ions, C_3S^{++} and C_4S^{++} , from such an isomer.

Can $C_4S_2^{++}$ also be successfully reduced to the as yet unknown neutral molecule C_4S_2 ? The answer is unequivocally yes. The neutralization-reionization mass spectrum (Figure 4) not only contains a quite intense signal for a "survivor" species C_4S_2 ; also all the other fragments in the NR spectrum can be readily assigned and are, again, best compatible with a linear connectivity $S=(C_x)=S$ for the neutral C_4S_2 whose lifetime t is at least $> 1 \mu s$ (determined by the time of flight from the first to the second collision chamber). In view of the fact that C_3S_2 is already known¹⁷⁾, the present finding together with the previously reported²⁾ successful generation of C_2S_2 clearly support the view that the elusiveness of $S=(C_x)=S$ does not reflect an intrinsic instability of these species; in the gas phase, both the neutral molecules as well as their cation radicals are perfectly stable.

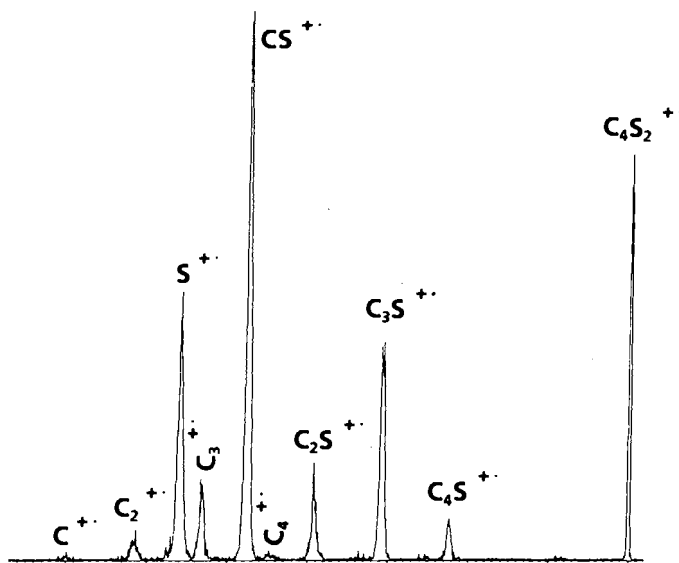


Figure 4. Neutralization-reionization mass spectrum of $C_4S_2^{++}$ ($m/z = 112$); Xe, 90% T//O₂, 90% T

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