observations, it is very likely that the failure of MFP method is gauge origin related.

The analysis of the computational time demanded by the analytic LMO and MFP methods would be in favor of the former method. In both methods, the Cartesian derivatives of the electric dipole moment (hence infrared intensities) are obtained in the same manner by using the analytic derivative methods. For obtaining the Cartesian derivatives of the magnetic dipole moment in the LMO method, all the needed parameters are already present in the calculation of the derivatives of the electric dipole moment, except that the expressions have to be recast in terms of the localized molecular orbital centroids. Since the conversion of canonical orbitals to localized orbitals requires only a trivial amount of computer time, the analytic LMO-VCD method (when successfully implemented) would require about the same time as that now required for the vibrational absorption intensities. In the MFP method, the magnetic dipole moment derivatives are obtained by solving the coupled Hartree–Fock (CHF) equations for magnetic field perturbation. In the DO gauge approximation the gauge origin has to be distributed among the N nuclei in the molecule and therefore the CHF equations for the magnetic field perturbation have to be solved N times. Thus the difference in the CPU time required for the MFP and LMO methods is the time required for the N CHF solutions of magnetic field perturbation versus that for localizing the orbitals once.

However, the important consideration is the reliability of predictions offered by a given theoretical method. This can only be determined when more calculations become available. For the LMO method, we have now completed the analysis of results[30-32] for *trans*-oxirane-*2,3-d*$_2$, *trans*-cyclopropane-*1,2-d*$_2$, methyloxirane, *trans*-2,3-dimethyloxirane, *trans*-2,3-dimethylthiirane, and methylcyclopentanone. In all these cases the agreement between the LMO-VCD predictions and the experimental observations is satisfactory.

Besides verifying the theoretical predictions against the experimental VCD observations, there is another way of assessing the predictive capabilities of a given VCD theory. Since the magnetic dipole moment derivatives are related[12] to the paramagnetic magnetizability, one can independently verify the VCD theories using the observed paramagnetic magnetizability. We have also done this comparison[33] for the paramagnetic magnetizability of oxirane, and the LMO predictions compared satisfactorily with the experimental data as well as with that obtained by the MFP method.[34]

5. Summary

Methylthiirane represents a challenging molecule for the theoretical VCD predictions. This is because the exact MFP method was unable to reproduce the experimetal spectrum satisfactorily due to the gauge related problems. The vibronic coupling VCD calculations are, at present, not feasible for methylthiirane, due to the need to augment a chosen basis set with the derivatized basis functions.

We have demonstrated that the ab initio LMO-VCD calculations are feasible and are in good agreement with the experimental observations for methylthiirane. A comparison of unscaled and scaled LMO-VCD predictions with the experimental results indicates that while VCD predictions obtained in the unscaled calculation are in satisfactory agreement with the experimental observations the literature scale factors[18] lead to incorrect frequency ordering for one pair of bands and to incorrect relative VCD magnitudes for some bands. This confirms our earlier conclusion[27] that the scaling method need not give better results than the purely ab initio results.

Although the normal mode displacements of orbital centroids were obtained numerically in the present calculations, they can be obtained by modifying the existing analytic methods for infrared intensities. We are currently planning to implement these analytic methods for VCD calculations, which would make the ab initio LMO-VCD predictions much more routine.

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Experimental Evidence for the Existence of Polycarbon Oxide Sulfides $O(C_n)S$ ($n = 3-5$) in the Gas Phase[†]

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Abstract: The elusive polycarbon oxide sulfides $O(C_n)S$ ($n = 3-5$) can readily be generated and structurally characterized in the gas phase by electron transfer reactions with use of neutralization–reionization mass spectrometry (NRMS). In addition, for $n = 3, 5$ both the radical anions and the radical cations are found to exist as stable species having the cumulene connectivity $O(C_n)S^{\bullet-/\bullet+}$. Similarly, the radical cation $O(C_4)S^{\bullet+}$ was structurally characterized as a cumulene. Common to all these species is a straightforward fragmentation pattern that allows an unambiguous structural assignment.

The recent interest[1] in linear and/or quasilinear molecules of the general structure $X(C_n)Y$ (X, Y = lone electron pair, H_2, O, S; $n \geq 2$) containing polycumulated double bonds is due to several factors. These species possess and/or are predicted to exhibit unique spectroscopic and chemical properties; in addition, their reactivity/stability properties as well as their electronic ground state (singlet versus triplet) follow an "odd/even" pattern. In fact, for the *odd*-numbered analogues of $X(C_n)Y$ ($n = 3, 5$) many

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[†] Dedicated to Professor Dr. Brigitte Sarry on the occasion of her 70th birthday.

(1) For an exhaustive literature coverage, see: Sülzle, D.; Beye, N.; Fanghänel, E.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 2069.

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combinations are known to exist for a long time. In distinct contrast, the *even*-numbered systems exhibit a reactivity such that, except for one case, they cannot even be produced as a transient under matrix conditions. However, this "instability" does not reflect an intrinsic property since under appropriate conditions several of these cumulenes could easily be generated. Typical examples include: CCS,[2] SCCS,[3] OCCS,[4] SCCCCS,[2] OCCCCO,[5] and SCCCCCCS,[1] which became accessible from their corresponding radical ions in the gas phase by using the powerful method of neutralization–reionization mass spectrometry (NRMS).[6] The fact that these and many other cumulenes[1] (except OC_4O[7]) remained undetected in the condensed phase while they appeared to be observable in the gas phase clearly indicates that their reported instability is due to facile *inter*molecular reactions. Moreover, some of these species were believed to play a crucial role in the genesis of interstellar organic molecules. A typical example corresponds to the triplet of :CCS which was recently detected[8] in interstellar clouds (Taurus Mol. Cloud-1, Sagittori B 2, IRC + 10216)[8] and later characterized[2] by NRMS as well as ab initio MO calulations[2,9] as a perfectly stable gas-phase molecule.

Following earlier studies on the gas-phase generation of OCCS[4] and $O(C_3)S$,[10] we will describe our findings on the higher homologues $O(C_n)S$ (n = 3–5). In contrast to the "symmetric" cumulenes $S(C_n)S$ and $O(C_n)O$, the mixed analogues $O(C_n)S$ possess a permanent dipole moment. These molecules are therefore ideal candidates for a detailed structural characterization by microwave spectroscopy,[10] thus guiding a radioastronomical search for these species.

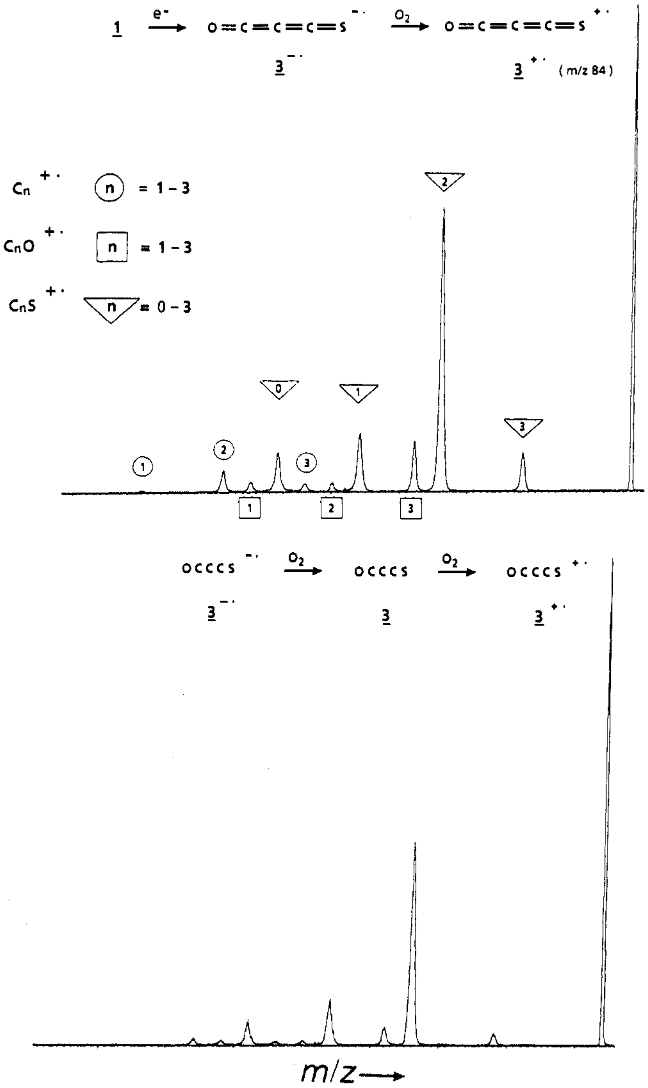

Figure 1. (a, top) CR spectrum of $OC_3S^{\bullet-}$ (m/z 84) (oxygen, 80% T); (b, bottom) NR spectrum of $OC_3S^{\bullet+}$ (m/z 84) generated from $OC_3S^{\bullet-}$ via CR (oxygen, 80% T//oxygen, 80% T)

Experimental Section

The mass spectrometric experiments were carried out with a modified VG Instruments ZAB mass spectrometer; this is a four-sector instrument of BEBE configuration (B stands for magnetic and E for electric sector). Positive ions are generated by 70-eV electron impact ionization of the literature-known precursors **1** and **2**, which were prepared and structurally characterized according to ref 11. Radical anions were generated in the negative ion mode with the same precursors (NH_3 is used as an electron moderation gas; $p \simeq 10^{-5}$ Torr). The following conditions were employed in the MS experiments: direct insertion probe, ion source temperature, 200 °C; ion trap current, 100 μA; accelerating voltage, 8 kV. Collision-induced dissociations (CIDs),[12] used to characterize the primary ions $M_1^{+/-}$, were brought about by mass-selecting a 8-keV beam of $M_1^{+/-}$ by means of B(1)/E(1) and colliding it with helium in a collision chamber located in the third field-free region (80% transmittance, T). Ionic products were recorded by scanning B(2). The second electric sector E(2) was not used in this experiment. Charge reversal (CR) experiments[12,13] were conducted by colliding the beam of mass-selected anionic precursors M_1^- with oxygen (80% T) and recording the positively charged fragment ions M_i^+ by scanning B(2). In the NRMS experiment, a beam of mass-selected M_1^+ ions (having 8-keV translational energy) was neutralized in the first cell of a differentially pumped tandem collision cell (located in the third field-free region) by colliding the beam with xenon (80% T). Unreacted ions were deflected away from the beam of neutral species M_i by putting a voltage of 500 V on a deflector electrode; subsequent reionization $M_i \rightarrow M_i^{\bullet+}$ occurred in the second collision cell by collision with oxygen (80% T). The resulting mass spectra were obtained by scanning B(2). If anionic precursors were subjected to a CR/NRMS experiment the combination $O_2//O_2$ as collision gases turned out to be the most superior one (80% T//80% T). The minimal lifetime t (identical with the transit time from the first to the second collision cell) in the present study is of the order of ca. 1 μs. For a schematic and a more detailed experimental description, see ref 3. In all MS experiments, signal-averaging techniques were used to improve the signal-to-noise ratio; 20–30 spectra were accumulated by on-line

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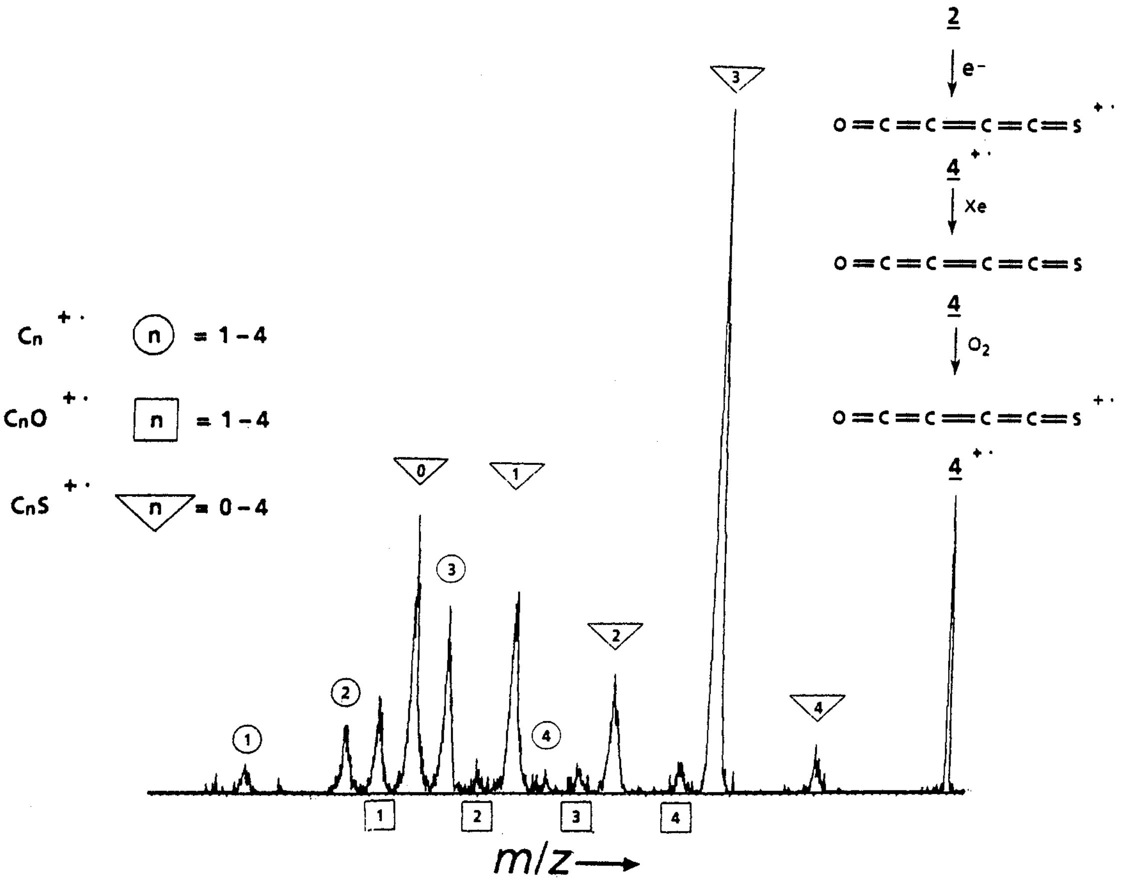
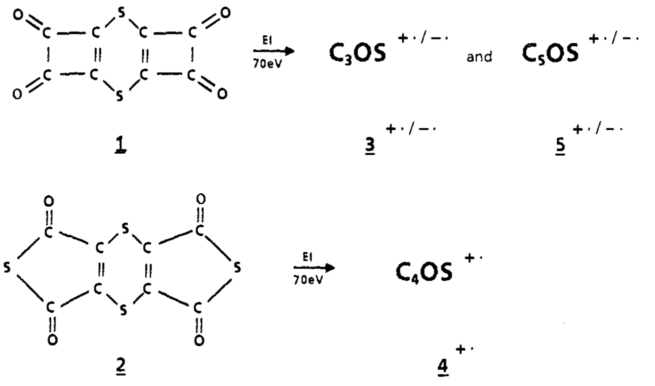


Figure 2. NR spectrum of $OC_4S^{\bullet +}$ (*m/z* 96) generated from **2** (xenon 80% T//oxygen, 80% T).

Scheme I



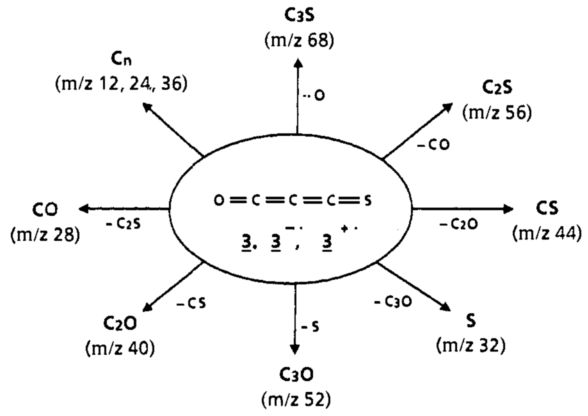
processing of the data with the VG 11/250 or the AMD-Intectra data system.

Results and Discussion

The radical cations and anions of C_3OS (*m/z* 84) and C_5OS (*m/z* 108) are easily accessible by dissociative ionization of **1**; for the generation of $C_4OS^{\bullet +}$ (*m/z* 96) the dithioanhydride **2** turned out to be the most suitable precursor (Scheme I). $C_4OS^{\bullet -}$ is also available from **2**; however, its signal intensity is too weak to permit further tandem mass spectrometric experiments. While the formations of $C_3OS^{\bullet -/\bullet +}$ (from **1**) and $C_4OS^{\bullet +}$ (from **2**) are likely to occur without skeletal reorganization of the ionized precursors, the generation of $C_5OS^{\bullet +/\bullet -}$ from **1** requests substantial isomerization of $\mathbf{1}^{\bullet +/\bullet -}$ prior to dissociation; the details are unknown.

(1) 3-Thioxo-1,2-propadien-1-one (O=C=C=C=S, 3) and Its Radical Ions $\mathbf{3}^{\bullet -/\bullet +}$. The special place occupied by tricarbon oxide sulfide OC_3S (**3**) among linear polycumulated double bond containing molecules is reflected in several studies: The first synthesis and microwave characterization of **3** by the Winnewisser group[10a-e] was followed by its gas-phase synthesis via pyrolysis combined with a PE-spectroscopic identification by Bock et al.[10f]

Scheme II



In 1983 Turner reported[10g] a tentative identification of OCCCS in interstellar medium. As will be demonstrated in the following, under our experimental conditions **3** as well as its hitherto unknown radical anion $\mathbf{3}^{\bullet -}$ and radical cation $\mathbf{3}^{\bullet +}$ are easily accessible from **1**, and the connectivity of these molecules is clearly reflected in the various collision-induced dissociations of these species. The general fragmentation pattern is depicted in Scheme II, and we note that all fragment ions can be assigned in an unequivocal way. For the sake of brevity we will not reproduce all spectra (which are available from the authors upon request) but rather confine the presentation to data of two experiments. (i) Dissociative electron attachment of **1** gives rise to $OC_3S^{\bullet -}$ (*m/z* 84). If this species is mass-selected and subjected to a charge reversal (CR) experiment, we obtain the spectrum shown in Figure 1a. Obviously, charge reversal gives rise to a detectable recovery signal for the radical cation *m/z* 84 ($OC_3S^{\bullet +}$); in addition, a fragmentation pattern results from which the connectivities of $OC_3S^{\bullet -}$ are immediately derivable. We should like to mention briefly two further experiments: If $OC_3S^{\bullet +}$, directly generated from **1**, is

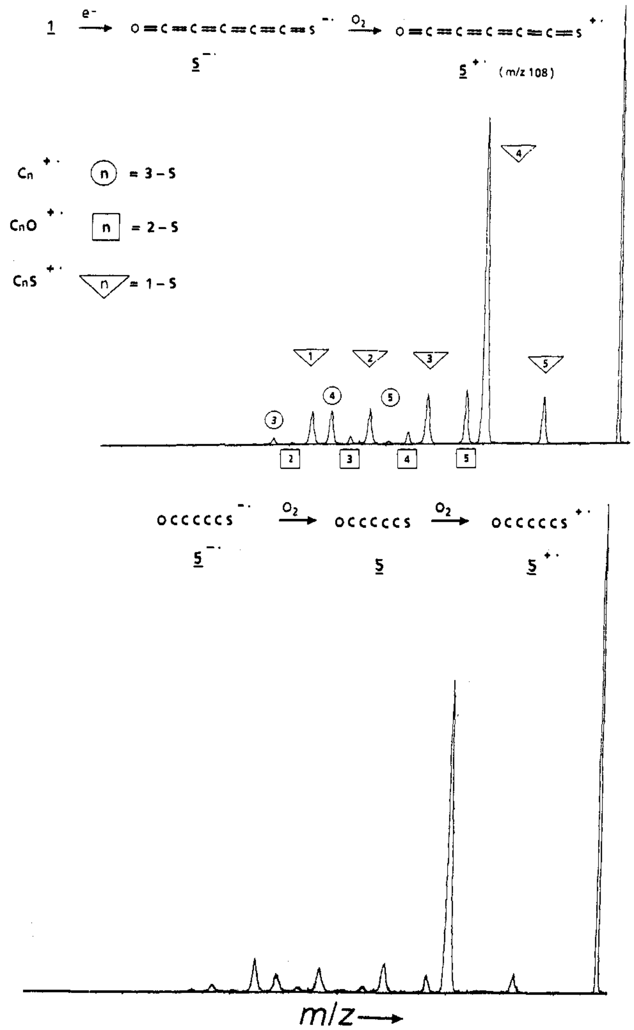


Figure 3. (a, top) CR spectrum of $OC_5S^{\bullet-}$ (m/z 108) (oxygen, 80% T): (b, bottom) NR spectrum of $OC_5S^{\bullet+}$ (m/z 108) generated from $OC_5S^{\bullet-}$ via CR (oxygen, 80% T//oxygen, 80% T).

subjected to a CA experiment, the fragmentation pattern is practically identical with the one shown in Figure 1a. In addition, if a beam of the radical anion $OC_3S^{\bullet-}$ is collided with helium, the CA spectrum (not shown) is, except for some intensity variation, again identical. Thus, we conclude that the species $OC_3S^{\bullet-}$ and $OC_3S^{\bullet+}$ correspond to the radical ions of tricarbon oxide sulfide $O{=}C{=}C{=}C{=}S^{\bullet+/\bullet-}$ ($3^{\bullet+}/3^{\bullet-}$).

Reduction of $OC_3S^{\bullet+}$ (formed via CR of $OC_3S^{\bullet-}$) in a NRMS experiment yields a recovery signal at m/z 84 as shown in Figure 1b. The fragmentation behavior is virtually identical with the one reported in Figure 1a. An identical spectrum (not shown) is also obtained if $OC_3S^{\bullet+}$ (generated directly from **1**) is subjected to a NR experiment. Thus, we conclude that the neutral tricarbon oxide sulfide ($O{=}C{=}C{=}C{=}S$, **3**) is indeed a stable gas-phase molecule, as reported earlier.[10] A further tandem experiment was conducted which consists of the sequence given in eq 1.

$$\mathbf{1} \xrightarrow{\text{EI}} OC_3S^{\bullet-} \xrightarrow{\text{CR}} OC_3S^{\bullet+} \xrightarrow{\text{NR}} OC_3S^{0/\bullet+} \xrightarrow{\text{CA}} \text{fragment ions} \quad (1)$$

The CA spectrum (helium) of reionized OC_3S (**3**) was found to exhibit the same spectral feature as shown in Figure 1b. Thus, we can safely state that Figure 1b is not signficantly affected by interference signals due to reionization of neutral fragment species.

(2) 4-Thioxo-1,2,3-butatrien-1-one (Tetracarbon Oxide Sulfide, $O{=}C{=}C{=}C{=}C{=}S$, 4) and Its Radical Cation $4^{\bullet+}$. The radical cation $\mathbf{4}^{\bullet+}$ can be made by dissociative ionization of **2**. Its CA mass spectrum (helium, 80% T) is, again, dominated by loss of CO; in addition, we observe all the fragments one would expect for a cumulene, i.e. $C_4S^{\bullet+}$ (13% of base peak), $C_3S^{\bullet+}$ (100), $C_4O^{\bullet+}$ (28), $C_2S^{\bullet+}$ (36), $C_3O^{\bullet+}$ (16), $C_4^{\bullet+}$ (6), $CS^{\bullet+}$ (32), $C_2O^{\bullet+}$ (3), $C_3^{\bullet+}$ (28), $S^{\bullet+}$ (37), $CO^{\bullet+}$ (4), $C_2^{\bullet+}$ (5), $O^{\bullet+}$ (2), $C^{\bullet+}$ (1). The NR mass spectrum (xenon/oxygen) of $OC_4S^{\bullet+}$ is given in Figure 2. We note the abundant recovery signal at m/z 96 and the fragmentation pattern typical for cumulenes. Thus, we conclude that the hitherto unknown *even*-numbered tetracarbon oxide sulfide **4** and its radical cation $\mathbf{4}^{\bullet+}$ are stable molecules in the gas phase. Sensitivity problems prevented us from structurally characterizing the radical anion $OC_4S^{\bullet-}$ which is also formed, though in low yield, from **2**.

(3) 5-Thioxo-1,2,3,4-pentatetraen-1-one (Pentacarbon Oxide Sulfide, $O{=}C{=}C{=}C{=}C{=}C{=}S$, 5) and Its Radical Ions $5^{\bullet-}$ and $5^{\bullet+}$. For **5** we were able to successfully conduct *all* the collision experiments already described above for **3** and its radical ions $\mathbf{3}^{\bullet+/\bullet-}$. Thus, it may suffice to simply represent the CR spectrum of $OC_5S^{\bullet-}$ (Figure 3a) and the NR mass spectrum (Figure 3b) of $OC_5S^{\bullet+}$, formed via charge reversal of $OC_5S^{\bullet-}$. Again, in addition to intense recovery signals we observe fragment ions that do not leave any doubt as far as the connectivity is concerned. We, therefore, conclude that the hitherto unknown cumulene OC_5S (**5**) and its radical anion $\mathbf{5}^{\bullet-}$ and radical cation are also stable in the diluted gas phase.

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