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Gas-phase reactivity of sulphur ions with ammonia

Gereon Niedner-Schatteburg, Thomas Schindler, Christian Berg, Dirk Wössner, and Vladimir E. Bondybey
Institut für Physikalische und Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

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The gas-phase reactions of sulphur cluster ions, cations S_n^+ ($n=1,...,8$) and anions S_n^- ($n=2,...,6$) with NH_3 have been studied by means of a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Relative and absolute reaction rate constants as well as reaction efficiencies have been determined. The S_4^+ cation has by the far highest reactivity with all other sulphur cations being significantly less reactive. Besides some fragmentation, no reactivity of the anions was found. Structural conclusions are made based on the present experiments, on previous extensive *ab initio* calculations, and on complementary experiments.

I. INTRODUCTION

The importance of sulphur chemistry and compounds for industrial applications as well as for biological and environmental aspects can hardly be overstated.[1] Liquid and solid elemental sulphur seems to exist in a large variety of allotropes. Gaseous sulphur consists mainly of S_8 rings at low temperatures ($T<400$ K) and of S_2 dimers at high temperatures ($T>1000$ K) with varying abundance of the intermediate sizes S_3–S_7.[2,3] Mass spectrometric investigations of sulphur vapor by electron impact ionization[2–6] and photoionization,[7,8] respectively, showed S_2^+ and S_8^+ to be abundant, but no larger species were found, while there were considerable amounts of S_3^+ to S_7^+. The relative intensities of the particular ions depend on ionization energy and temperature of vaporization.

Neutral sulphur clusters S_n with $n\geqslant 6$ are proved experimentally to have ring structures.[9] Theoretical information on all of the sulphur clusters up to $n=13$ can be found in recent publications. Semiempirical calculations have been performed for S_3–S_8.[10,11] Extensive calculations have been performed on S_6–S_{12} (Refs. 12 and 13), and particularly on S_4 (Refs. 14 and 15) using large scale *ab initio* methods. The structures of S_2–S_{13} have also been determined by a procedure called stimulated annealing calculations.[16] These theoretical studies also concluded that clusters with $n\geqslant 5$ should exist as ring structures; the smaller ones S_3 and S_4 may exist as rings and chains as well. In Raman spectroscopy investigation of superheated sulphur vapor, two distinct conformers of S_4 have been identified by their vibrational modes.[17] The C_{2v} symmetry of S_3 and of its anion S_3^- have also been confirmed.[17(a)] S_4 exists in *cis* and *trans* planar structures and is distinctly different from $(S_2)_2$ dimers, as was shown in recent matrix isolation studies.[18,19] The C_{2v} S_3 has also been investigated in these studies. Almost no structural information is available for the cations so far. The S_5^+ cation is known to be stable in solution and is likely to be planar and cyclic with the unpaired electron in a π orbital.[20] Sulphur in liquid ammonia reacts to form S_3^-, S_6^{2-}, S_2N^-, S_3N^-, and S_4N^-.[21]

The gas-phase reactivity of atomic sulphur cations has previously been extensively investigated (for a compilation see Refs. 4 and 22). In an ion cyclotron resonance (ICR) study, an absolute rate constant of 1.25×10^{-9} cm^3 s^{-1} has been determined for their reaction with NH_3 yielding mostly (94%) NH_3^+ besides some SNH_2^+ (6%). A later investigation confirmed these values in general [1.6(3) $\times10^{-9}$ cm^3 s^{-1}, 90% and 10%, respectively].[24] High pressure flowing afterglow and selected-ion-flow-tube (SIFT) investigations[25,26] concluded in comparable rate constants of $1.4\times10^{-9}\pm30\%$ and 1.7×10^{-9} cm^3 s^{-1}, respectively, but failed to observe the minor product SNH_2^+.

In a continuation of our investigations of the gas phase chemistry of sulphur cluster ions,[4,27,28] the reactivity with NH_3 has been studied using a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.[29–32] The absolute reaction rates obtained for both cations and anions are compared to the theoretical collision rate limit[33–35] to extract reaction efficiencies.

II. EXPERIMENTAL SETUP AND METHOD

A commercial FT-ICR spectrometer (Spectrospin CMS 47 X) equipped with a 4.7 T superconducting magnet, a cylindrical 60×60 mm ICR cell, and a differentially pumped external ion source[32,36–39] was used as described earlier.[4,27] Sulphur cluster ions S_n^+ and S_n^- were generated by electron impact ionization (70 eV) of sulphur vapor and subsequent electron attachment, respectively. Resulting cations sized $n=2$–8 and anions sized $n=2$–6 were transferred into the ICR cell and trapped. Monomeric sulphur ions did not form this way, but could be prepared from suitable molecular precursors. Initial kinetic energies of the ions under conditions of our experiments are 3.8 ±0.5 eV. Both translational and internal degrees of freedom were thermalized within 2 s by collisions with the ambient reactive NH_3 gas introduced into the apparatus via a needle valve and held at a pressure of 6×10^{-8} mbar (uncorrected). The specific sulphur cations or anions to be investigated, respectively, were then isolated in the ICR cell by ejecting all the unwanted ions.

Detection of product ions and remaining parent ions occurred after a variable reaction delay by means of a standard detection cycle, consisting of a fast rf chirp over the range of all frequencies of interest, digitizing of the ionic response, and fast Fourier transform (FFT) processing

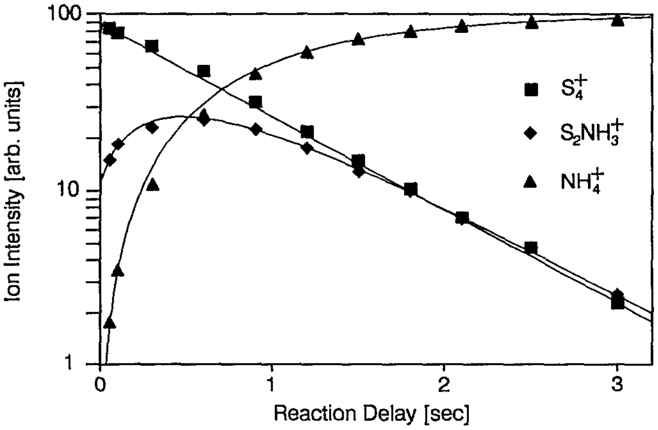


FIG. 1. Concentration profiles of $S_4^+ + NH_3$ reactions. Experimental data for S_4^+, $S_2NH_3^+$, and NH_4^+ have been fitted by pseudo-first order kinetic equations (solid lines) while optimizing the rate constants of the consecutive reactions $S_4^+ + NH_3 \rightarrow S_2NH_3^+ + NH_3$ and $S_2NH_3^+ + NH_3 \rightarrow [S_2 + NH_2] + NH_4^+$, respectively.

TABLE I. Total absolute reactive rate constants and efficiencies of various sulphur cations and anions with ammonia. The relative rate constants of the FT-ICR measurements were scaled to the well-known proton transfer cross sections of $NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$ (Refs. 41 and 42). Reaction efficiencies were obtained by comparison of the experimental data to the theoretical capture rate limit as given by the average dipole orientation theory (Refs. 33–35).

Reaction	k (10^{-10} cm^{3}s^{-1})	Efficiency (%)
$S^+ + NH_3 \rightarrow S + NH_3^+$	11.7,[a] 14.4,[b] 13	62,[a] 76,[b] 65
$\rightarrow SNH_2^+ + H$	0.8,[a] 1.6,[b] 0.85	4,[a] 8,[b] 4.3
$S_2^+ + NH_3 \rightarrow S_2 + NH_3^+$	0.015 ± 0.006	0.08 ± 0.03
$S_3^+ + NH_3 \rightarrow S_3 + NH_3^+$	0.10±0.05	0.6±0.3
$S_4^+ + NH_3 \rightarrow S_2NH_3^+ + S_2$	3.8 ± 0.8	22 ± 5
$S_2NH_3^+ + NH_3 \rightarrow S_2NH_2 + NH_4^+$	7.2 ± 1.5	42 ± 9
$S_n^+ + NH_3 \rightarrow \cdots$ ($n=5,...,8$)	<0.01	<0.06
$S_n^- + NH_3 \rightarrow \cdots$ ($n=2,...,6$)	<0.01	<0.06

[a] Rates have been calculated from total rates and branching ratios of Ref. 23. Efficiencies originate from the comparison of these rates to the collision rate as predicted by the ADO theory (Refs. 33–35).

[b] The same as in footnote a, but based on experimental data of Ref. 24.

with consecutive magnitude calculation and mass scale linearization. Numeric peak height evaluation of the observed mass peaks finally yields intensities of the various ions as a function of reaction delay (Fig. 1). Relative, pressure dependent reaction rates were extracted from these data by a numerical fitting procedure assuming pseudo-first order kinetics as will be described elsewhere.[28] Numerous previous publications give detailed descriptions of FT-ICR instruments and of the principles of their operation.[29–32,36–40]

In order to calculate the absolute rate constants, an independent pressure calibration was needed. No attempt was made to determine the number density of the NH_3 gas in the ICR cell directly as too many uncertainties enter. Instead, the rate constant[41,42] of the extensively studied proton transfer reaction

$$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2 \qquad (1)$$

was used to accomplish the pressure calibration. By comparison of our measured relative rate for reaction (1) to the absolute literature value, we obtained the number density of the NH_3 reactive gas inside the ICR cell. The ratio of this value, converted to a gas pressure, and of the uncalibrated ion gauge reading was a linear pressure reading correction factor in all of the following evaluations. Thus the appropriately scaled pressure reading was applied to the relative rate constants of the $S_n^+ + NH_3$ reactions putting those on an absolute scale. The estimated uncertainty in the absolute value is ±20%. The relative values of rate constants within the present investigation itself are believed to be accurate to ±5%.

In addition, we compared literature values on $S^+ + NH_3$ reactions[23,24] with data evaluated by the use of the above discussed pressure calibration (cf. Table I). Our total reaction rate of 14×10^{-10} cm^{3}s^{-1} fits reasonably well with the previous values of 12.5 (Ref. 23) and 16×10^{-10} cm^{3}s^{-1},[24] respectively. Since the literature values disagree with respect to both the absolute rate constants and the branching ratios of the two reactions occurring, we have not attempted to improve our pressure calibration by using the S^+ reaction, but used the more unambiguous data on proton transfer of ammonia ions.

III. RESULTS AND DISCUSSION

As noted above, vaporization of sulphur, followed by electron impact ionization, permitted the generation of mass selected cations with two to eight atoms and of anions with two to six atoms. The observed reactions of these ions with ammonia are summarized in Table I. Pseudo-first order kinetics were used to evaluate the relative rate constants. Total rate constants were calculated from these data using the pressure calibration as outlined above.

No detectable reactions of any of the anions S_n^-, $n=2,...,6$, with ammonia were observed. The absence of observable products under our experimental conditions yields only upper limits for the overall reaction rate constants and these are listed in Table I. Some of the otherwise unknown electron affinities have been determined experimentally by other groups to 1.663±0.040 eV for S_2,[43] 2.093±0.025 eV for S_3,[44] and by means of high level *ab initio* calculations to 1.9–2.7 eV for S_4.[15] It is well known that NH_4^- and NH_3^- are not stable, while the electron affinity of NH_2 is 0.74 eV.[45] Thus electron transfer of small sulphur anions to ammonia is too endoergic to take place. As we do not see any products for larger sulphur anions, we conclude that the electron affinity of these is about equally high. In liquid ammonia, sulphur is known to form S_4N^- by reaction with four NH_3.[21] Under single collision conditions, this reaction does not proceed. In summary, we have no evidence of any reactive gas phase process taking place for $S_n^- + NH_3$, $n=2,...,6$.

Among the cations, the larger species S_5^+ to S_8^+ are virtually inert as well. While at short times a small amount of fragmentation of the more energetic ions is observed, after the two second collisional thermalization, no further reactions are detected.

Sulphur monomer cations S^+ were obtained by 70 eV electron impact ionization of CS_2 in the external ion source and subsequently transferred into the ICR storage and analysis cell. Previous studies have concluded that S^+ reacts with ammonia molecules via charge transfer efficiently.[23,24] We compared these published reaction rates with theoretical values calculated by us from the average dipole orientation (ADO) theory.[33–35] These values were taken as a theoretical capture rate limit. The ratio of the experimental results to the ADO theoretical rates can be viewed as the efficiency of the reactive process per collision. Thus, we interpret the previous data in terms of a charge transfer efficiency of 62% (Ref. 23) and 76% (Ref. 24) per collision, respectively. Our result of 65% of the collision rate is in good agreement with these existing works. The results also agree well with the known ionization potentials of 10.36 and 10.15 eV (Ref. 46) for S and NH_3, respectively. Thus charge transfer in $S^+ + NH_3$ collisions is exoergic by about 210 meV. This type of near resonant charge transfer is a long range process to proceed almost with collision rate as indeed observed.

S_2^+ and S_3^+ both exhibit little charge transfer reactions with ammonia, with the latter cation being somewhat more reactive

$$S_n^+ + NH_3 \rightarrow S_n + NH_3^+ . \qquad (2)$$

The reactivities of S_2^+ and S_3^+ are relatively poor, in both cases less than 1%. Reaction (2) is detectable for $n=2$ and 3, but is not observed for the larger species. Thus we conclude that the ionization potentials of sulphur clusters with $n > 4$ are significantly smaller than that of ammonia 10.15 eV.[46] In fact, this has been proven to be the case.[5,7,8] The ionization potentials for S_5–S_8 all range from 9 ± 0.4 eV. The ionization potential of S_2 is well determined by photoionization experiments and by theoretical investigations to be 9.36 ± 0.02 eV.[7,8] This agrees acceptably with the somewhat higher value of 9.6 eV from the most recent electron impact investigations.[5] In any case, charge transfer in near thermal $S_2^+ + NH_3$ collisions is unlikely to take place due to the endoergicity of 0.8 eV. Nevertheless, a small amount of NH_3^+ products was observed. We conclude that either vibrational or translational energy of S_2^+ accounts for this enhanced reactivity.

Berkowitz *et al.* have also measured by photoionization the ionization potential of S_3 to be 9.68 ± 0.03 eV.[7,8] In contrast, more recent electron impact ionization experiments conclude in a considerably higher value of 10.2 eV.[7,8] Our present investigation showing little charge transfer (less than 1% of the collision rate) in $S_3^+ + NH_3$ casts some doubt about the latter results. Based on the near absence of charge transfer in the present work, we can conclude that the adiabatic ionization potential of S_3 is considerably lower than that of NH_3.

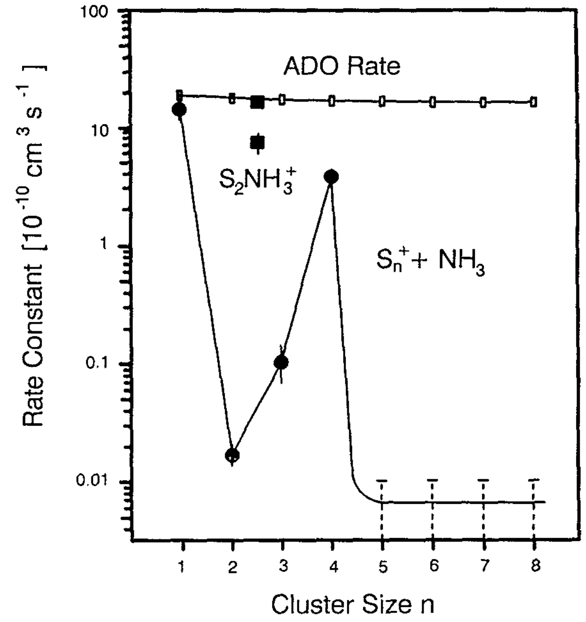


FIG. 2. Absolute rate constants for the reaction of size selected sulphur cations S_n^+, $n = 1,...,8$ with ammonia. The capture rate limit as predicted by the average dipole orientation theory (ADO) is shown for comparison. The rate constant and capture limit, respectively, of the secondary reaction $S_2NH_3^+ + NH_3 \rightarrow [S_2 + NH_2] + NH_4^+$ are also included.

Among the cations studied here, S_4^+ is by far the most reactive. It is also the only one of the sulphur ions which exhibits a "genuine" chemical reaction. Its reaction and the time evolution of its product are presented graphically in Fig. 1. It reacts according to the equation

$$S_4^+ + NH_3 \rightarrow S_2NH_3^+ + S_2 . \qquad (3)$$

That is, it eliminates S_2 and forms the adduct ion $S_2NH_3^+$. This reaction is rather rapid with an efficiency of more than 20% per collision (Table I). The $S_2NH_3^+$ ion itself is not a final product, but it reacts further by proton transfer to ammonia

$$S_2NH_3^+ + NH_3 \rightarrow NH_4^+ + [S_2 + NH_2]. \qquad (4)$$

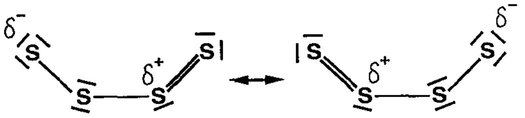
Here the brackets account for our lack of knowledge of the exact identity of the neutral products. Unbound S_2 and NH_2 are assumed to be most likely based on simple energetic reasons, nevertheless. The rate with which reaction (4) proceeds, as compared to the collision rate, yields a reaction efficiency of $42\% \pm 9\%$ per collision. This is twice as high as in the case of reaction (3). It can also be compared with the efficiency of proton transfer from naked NH_3 $89\% \pm 9\%$.

As already noted above, the observed reactions are summarized in Table I, and the overall sulphur cluster cation reactivities are represented graphically in Fig. 2. It can be observed that while S_2^+ and S_3^+ react rather slowly by charge transfer to ammonia, the S_4^+ cation reacts nearly two orders of magnitude faster, with a rate approaching the collisional rate. The still larger S_n^+ ions are then unreactive with their respective reaction rates being at least three orders of magnitude slower.

IV. S_4^+ STRUCTURE AND ITS REACTIVITY WITH NH_3

The structure of S_4^+ has not previously been determined either experimentally or theoretically. In contrast, the neutral tetrasulphur S_4 has been the subject of many theoretical[12–16] and experimental[17–19] investigations. The focus onto S_4 stems from its ambiguous structure with the possibility of many isomeric species. The most extensive and almost exhaustive study of all isomers and possible geometries[14] concluded that open chain structures *cis* C_{2v} and *trans* C_{2h} are energetically favored. Also a rectangular D_{2h} structure resembling $(S_2)_2$ bound side by side should be very low in energy. True closed cyclic forms such as square planar and puckered rings D_{4h} and D_{2d}, respectively, are found considerably higher in energy. A subsequent study involving the same structures and increased basis sets agreed with these findings.[15] The definite experimental detection of two different but related isomers of S_4 in Ar matrix spectra ruled out the D_{2h} isomer and assigned two strong infrared bands to the ν_5 asymmetric stretch of the *cis* and *trans* isomers in good agreement with the scaled *ab initio* frequencies.[18] Both isomers are said to contain two pairs of equivalent S atoms based on the analysis of vibrational band multiplets. A more recent matrix isolation study on electronic transitions in the visible region conclude in strong evidence for a *cis* planar ↔ branched ring (C_s) photoisomerization, which is in partial disagreement with the conclusion of the previous study.[19] Nevertheless, both studies agree in the *cis* planar C_{2v} isomer as the lowest energy conformer of neutral S_4.

Previous x-ray diffraction experiments have been interpreted to show that open sulphur chains with more than four atoms possess terminal bonds which are strengthened with respect to single S–S bonds.[47] Typical terminal bond lengths range ~ 1.95 Å compared with a typical S–S single bond as in long sulphur chains of 2.06 Å (Ref. 1) or with a typical S=S double bond length as in S_2 of 1.889 Å.[46] These terminal bonds thus seem to have partial double bond character. Simultaneously, the neighboring bonds will be weakened.[47,48] In the case of S_4 chains, this implies a substantially weakened central bond framed by two strong terminal bonds. Valence bond considerations come to the same conclusion, while the two resulting structures below are meant as resonance structures only



It was suggested before[14] that any other possible choice of valence structures violates the semiempirical rules. The SCF-level optimized bond lengths are in agreement with the predicted strong–weak–strong pattern, confirming some double bond character of the terminal bonds, while the central bond in the *cis* S_4 chain is greater than the typical single bond length. The averaged distribution of the partial charges δ^+ and δ^- yields a considerable dipole moment indeed confirmed to be 1.73 D at the highest level of *ab initio* theory applied.[14]

Application of molecular orbital treatment to the four atomic *p* orbitals perpendicular to the σ-bonded *cis* skeleton plane reveals a system of π orbitals resembling that of *cis* butadiene.[14] The highest, doubly occupied molecular orbital is of b_1 symmetry. It has mainly the character of a nonbonding lone pair centered at either of the terminal sulphur atoms. Ionization corresponds to the removal of one of these electrons $S_4\ {}^1A_1 \rightarrow S_4^+\ {}^2B_1$. It is not clear to what extent this ionization would induce an electronic and geometrical reorganization. For the present discussion, it is assumed that the S_4^+ cation remains basically in the electronic and geometric structure of its neutral parent molecule. It is mainly the uneven strong–weak–strong bond strength pattern that is expected to occur in the neutral tetrasulphur as well as in the cation. Possible *d*-orbital contributions potentially complicating the present picture are generally believed to be of marginal significance.[49]

The *ab initio* calculated ionization potentials depend only weakly on the geometric structures yielding 8.7 (Ref. 14) and 8.5 eV,[15] respectively, for the *cis* S_4 isomer. The only experimental, electron impact investigation lists 10.1 eV.[5] Our present FT-ICR investigation did not observe any charge transfer in collisions of S_4^+ with gaseous NH_3 molecules which have an I.P. of 10.15 eV.[46] The high energy tail of a 300 K thermal Maxwell–Boltzmann distribution would easily compensate for the endoergicity of charge transfer of only 50 meV. Thus, we conclude that the true ionization potential is considerably lower than presumed in Ref. 5. Whether the ionization potential is as low as calculated in Refs. 14 and 15 has to be checked separately, e.g., by means of charge transfer bracketing investigations as was recently performed for arsenic and phosphorous clusters.[50]

The present investigation observed efficient cleavage of S_4 clusters by ammonia molecules according to Eq. (3). No asymmetric bond rupture in favor of S or S_3 containing products was observed. This seems to support the *cis* S_4^+ structure as outlined above and the presumed strong–weak–strong bond strength pattern. Moreover, the anticipated charge distribution and even the molecular dipole of S_4^+, though certainly reduced with respect to the calculated value for S_4 upon ionization, favor the head-on nucleophilic attack of the nitrogen lone pair into the central weak bond of the S_4^+ chain. Thus, it could well be that the observed reaction efficiency of only 22% simply reflects a steric factor of an otherwise direct reaction. Of course, our experimental investigations are not sensitive to a *cis* to *trans* isomerization of S_4^+ chains. Nevertheless, the observed reaction with NH_3 appears to exclude true cyclic structures for S_4^+ cluster cations in agreement with all *ab initio* calculations performed for neutral S_4 so far.

V. LARGE SULPHUR CLUSTER REACTIVITY

Larger sulphur cations S_n^+, $n \geqslant 5$ do not react observably with NH_3 under our experimental conditions. Our previous studies of reactions with NO_2 showed a similiar discontinuity at $n = 4$–5.[4,27] S_5^+, and all of the larger neutral sulphur clusters S_n^+, are known to occur preferentially in cyclic forms. Based on the arguments presented above, any chain-like cation isomers could be expected to possess strong terminal and weak near terminal bonds. Such structures should yield reactive cleavage in collisions with ammonia, which is not observed. We believe that the presence of open chain or helical isomers would be detected by their typical reaction products. Thus, significant amounts of those are excluded. The only confirmed large S_n^+, $n \geqslant 5$ isomers are closed and cyclic. These conclusions are consistent with our earlier investigations concerning the gas phase chemistry of sulphur cations S_n^+, $n=2,...,8$, with NO and NO_2. These showed a decreasing reactivity with a rising number of atoms with a minimum at $n=5$.

Very little can be said about the anions S_n^-, $n=2,...,6$ based on the present results. Neither electron transfer nor genuine *chemical* reactions are observed for any of the cluster sizes examined. Our previous studies of reactions with NO_2 (Refs. 4 and 27) have shown both electron transfer and chemical reactions, with rates varying slowly with cluster size. No break in reactivity was observed for the larger clusters. We tentatively suggest open chain type isomers for all anion sizes observed $n \leqslant 6$. Minor amounts of cyclic and thus unreactive larger cluster anions, however, are not excluded by our data. Nevertheless, we have no indication for those to occur.

VI. SUMMARY

Only the smallest cations studied (S_n^+, $n=2$–4) are found to react with NH_3. S_2^+ and S_3^+ exhibit slow charge transfer with NH_3. S_4^+ undergoes chemical reaction forming efficiently the $S_2NH_3^+$ product ion. This, in turn, reacts further, yielding ammonium ion NH_4^+ as a final product. Except for some fragmentation due to initial kinetic energy upon introduction into the ICR cell, the larger ions do not react. This is in contrast to the results of the NO/NO_2 investigations, where S_2^+ is most reactive and the reactivity decreases with increasing size. The overall reactivity with NH_3 exhibits a sharp maximum for $n=4$, while reactivity is more than two orders of magnitude smaller for all other sizes. Based on these results, we suggest open structures for S_3^+ and S_4^+, and closed rings for S_n^+, $n \geqslant 5$.

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