The Anomalous High Reactivity of Ca^+ with S_8 in the Gas Phase: $[CaS_3]^+$ and $[CaS_{11}]^+$

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The ion $Ca^+(g)$ reacts more rapidly than any other $M^+(g)$ with $S_8(g)$, first forming $[CaS_3]^+$, which undergoes reversible addition of S_8 to $[CaS_{11}]^+$, with slower formation of a second more stable isomer of $[CaS_{11}]^+$ believed from density functional calculations to have the structure $(\eta^2\text{-}S_3)Ca(\eta^4\text{-}1,3,5,7\text{-cyclo-}S_8)$.

Richly diverse metal–sulfur chemistry now encompasses innumerable clusters with metal sulfide cores,[1] a special $MoFe_7S_9$ cluster in nitrogenase which is the active site for the activation of N_2,[2] two-dimensionally non-molecular metal sulfides and their intercalates,[1,3] a plethora of metal compounds with polysulfide ligands,[4] elementary redox reactions of metals with sulfur mediated by amine solvents,[5] metal complexes with polythiane ligands,[6] bionanocrystallites,[7] and hundreds of gas phase negative ions $[M_xS_y]^-$ generated by laser ablation of metal sulfides.[1,8] We are investigating another facet, namely the fundamental reaction $M^+(g) + S_8(g)$ in the pristine gas phase,[9] devoid of supramolecular influences. We have investigated $M^+(g)$ from all of the Periodic Table,[10] but none reacts with $S_8(g)$ more rapidly than does $Ca^+(g)$.

Our reaction vessel is the ion trap of a Fourier Transform Ion Cyclotron Resonance (ICR) mass spectrometer. The $Ca^+(g)$ is generated by laser ablation of CaF_2, and S_8 pressure is maintained at 1×10^{-8} mbar by continuous vaporisation of the solid contained in a capillary adjacent to the CaF_2.

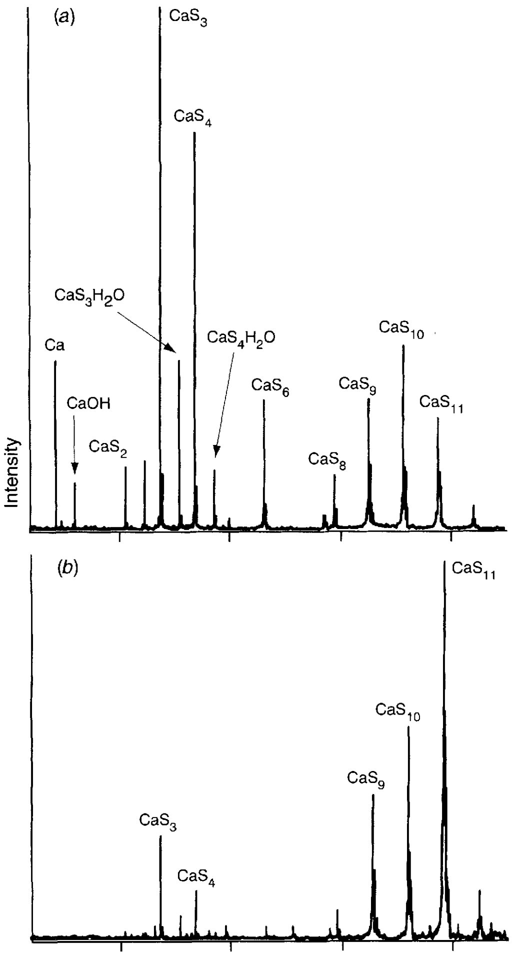


Fig. 1 Positive ions formed in the reaction of Ca^+ (all other ions ejected prior to reaction) with $S_8(g)$ at 1×10^{-8} mbar, after reaction periods of 1.5 s (*a*) and 2.5 s (*b*)

Mass spectra of the $Ca^+ + S_8$ reaction mixture (Fig. 1) show that Ca^+ is mostly converted to products at 1.5 s and is totally consumed after 2.5 s. This pseudo-first order rate of reaction with S_8 is about twice that of Mg^+, and exceeds the rates of Sc^+ and all of the first-row transition metals.[9] The closed-shell ion K^+ does not react with S_8.

In early stages of the reaction (*ca.* 1 s), $[CaS_3]^+$ is the dominant product, but it then diminishes rapidly in intensity as the larger ions $[CaS_9]^+$, $[CaS_{10}]^+$ and $[CaS_{11}]^+$ develop, with $[CaS_{11}]^+$ as the final product. The smaller ions $[CaS_2]^+$, $[CaS_3]^+$ and $[CaS_4]^+$ also scavenge adventitious water. The distribution of $[MS_y]^+$ products for Ca is different from the general pattern observed for other metals, in which the major first product is $[MS_4]^+$, growing with y even through 6, 8, 10, and with $[MS_{12}]^+$ as the largest and latest major product. The ions $[CaS_3]^+$, $[CaS_9]^+$ and $[CaS_{11}]^+$ have uncommon compositions, and thus the chemistry of Ca^+ with S_8 is different in product distribution as well as reactivity.

In order to probe the reaction patterns we have isolated individual $[CaS_y]^+$ products in the ICR cell, and examined their further reactivities in the presence of S_8. Isolated $[CaS_3]^+$ reacts with S_8 to form mainly $[CaS_9]^+$, $[CaS_{10}]^+$ and $[CaS_{11}]^+$. However, the steady growth of $[CaS_{11}]^+$ in this experiment, and evident also in Fig. 1, is deceptive, because when $[CaS_{11}]^+$ is isolated (in the presence of the background S_8) it undergoes rapid decomposition. Fig. 2 shows that $[CaS_{11}]^+$ is 90% dissociated within 2 s, to *ca.* 70% $[CaS_3]^+$ and *ca.* 20% $[CaS_9]^+$ in the same period. Evidently there is a fast process in which $[CaS_{11}]^+$ on collision with S_8 reverts to $[CaS_3]^+$ through loss of S_8. However, the concentration of $[CaS_{11}]^+$ decreases not to zero, but to a steady state and then slowly increases. This result, together with the steady increase of $[CaS_{11}]^+$ apparent in Fig. 1

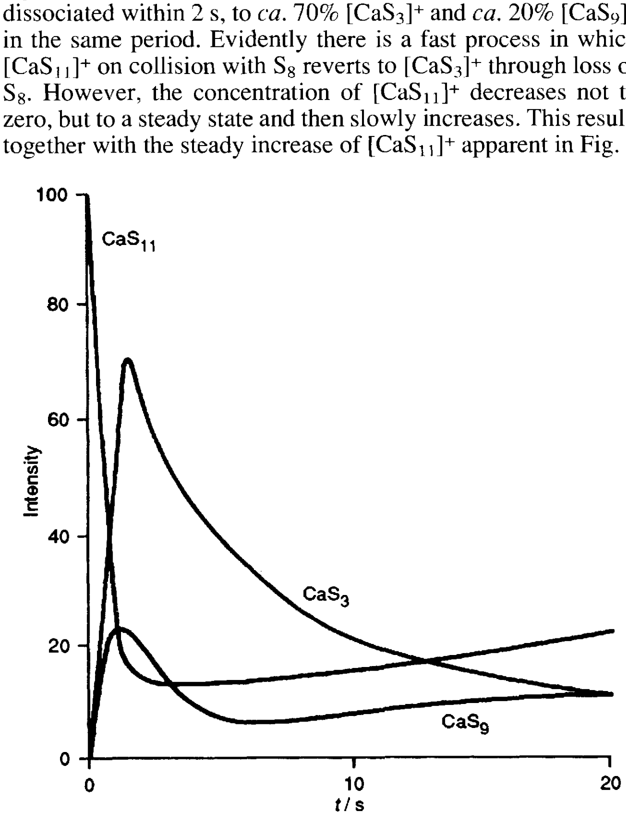


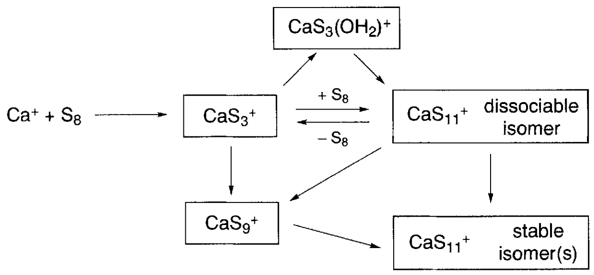
Fig. 2 Temporal evolution of the more abundant ions after isolation of $[CaS_{11}]^+$ in the presence of S_8 at 1×10^{-8} mbar. The $[CaS_{11}]^+$ was isolated 1 s after laser ablation, during which period more than one isomer of $[CaS_{11}]^+$ had been generated.

and all other experiments, indicates that there is at least one additional isomer of $[CaS_{11}]^+$.

Scheme 1 shows the transformations for $[CaS_3]^+$, $[CaS_9]^+$ and $[CaS_{11}]^+$. The $[CaS_{11}]^+$ observed at any time is a mixture of at least two isomers, one of which dissociates very rapidly to $[CaS_3]^+$ and another which is stable. Thus the reactivity experiment reported in Fig. 2 also begins with a mixture of isomers of $[CaS_{11}]^+$, and this has been confirmed by varying the total time between the laser ablation event and the isolation of $[CaS_{11}]^+$: as expected the apparent extent of rapid dissociation of $[CaS_{11}]^+$ to $[CaS_3]^+$ diminishes as the storage time of all $[CaS_{11}]^+$ increases.

Our understanding of the structures and reactivities of these ions is supported by explorations of the structure–energy surfaces using density functional computations, building on experimental and theoretical knowledge of S_y molecules:[11] some key results are summarised here.

Approach of Ca^+ towards S_8 in either of the directions shown in Fig. 3(*a*) allows total reduction in the total energy concomitant with scission of two S–S bonds and the separation of CaS_3 from S_5. These are believed to be collisional pathways for the observed rapid formation of $[CaS_3]^+$, while the less probable approach of Ca^+ close to the fourfold axis of S_8 forms $[CaS_8]^+$. The most stable structure for $[CaS_3]^+$ is the planar quadrilateral, Fig. 3(*b*). The Ca–S distances in $[CaS_y]^+$ are longer by *ca.* 0.4 Å than the longest M–S distances of transition metals in comparable $[MS_y]^+$. This, together with the reduced directionality of bonding to Ca, and the stability of orthogonal torsional angles in S–S–S–S chains, are principal factors in the distinctive structure–energy surface for $[CaS_y]^+$. Fig. 3(*c*) shows the approach of $[S_3Ca]^+$ to an S–S edge of S_8 which yields the easily dissociable isomer of $[CaS_{11}]^+$, while Fig. 3(*d*) illustrates a more stable isomer of $[CaS_{11}]^+$ resulting from facial (1,3,5,7) approach of $[S_3Ca]^+$ to S_8. Similar structural principles apply to $[CaS_9]^+$, for which the $[Ca(S_3)_3]^+$ structure shown in Fig. 3(*e*) is calculated to be the most stable. The main general conclusions are that the special character of the reactions of Ca^+ with S_8 derives from the ability of Ca^+ to extract and stabilise S_3 (as opposed to the extraction of S_2 and S_4 by transition metals), and from the retention of favourable cyclic S_y conformations (particularly crown S_8) in the products.



Scheme 1

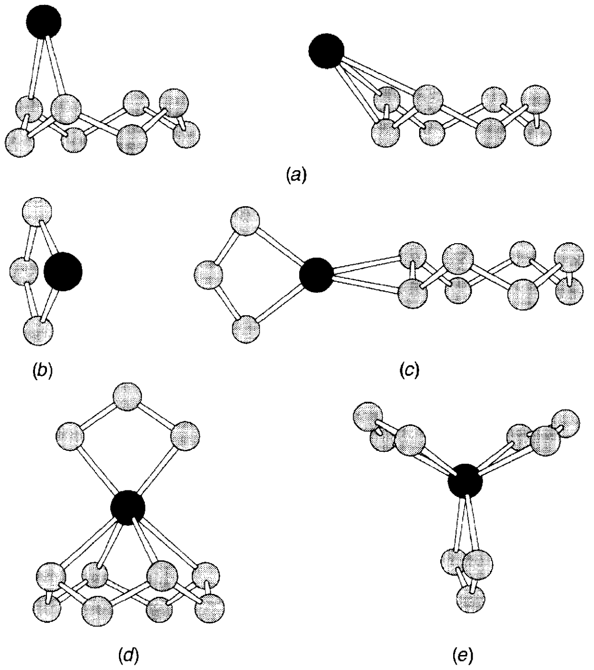


Fig. 3 Some significant structures for CaS_y^+ reactions and products. (*a*) Two of the approaches of Ca^+ to S_8 which on energy minimisation yield separate $[CaS_3]^+$ and S_5. (*b*) The most stable planar structure of $[CaS_3]^+$, Ca–S 2.63, 2.63, 3.14 Å; S–S 2.10, 2.10 Å. (*c*) The approach of $[S_3Ca]^+$ to the rim of S_8 to form a dissociable isomer for $[CaS_{11}]^+$. (*d*) The most stable isomer calculated for $[CaS_{11}]^+$: Ca–S in the CaS_3 segment are 2.71 Å, while Ca–S (cyclo-S_8) are 3.16, 3.20 Å. (*e*) The most stable structure calculated for $[CaS_9]^+$.

The high reactivity of calcium with sulfur in the gas phase provides a reference point for evaluation of the dominant influences of environment in the different patterns of reactivity and structure in condensed phase metal sulfur chemistry.

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