Supplementary Information

Energetics of the S^{2+} + Ar → S^+ + Ar^+ reaction

The ground state of S^+, ^4S lies 10.4 eV above the ground state of S(^3P). If only the ^3P, ^1D or ^1S states of S^{2+} are involved in a SET reaction with Ar, S^+ can be formed in one of four different electronic states, with energies of less than 21.3 eV above the ground state of S. However, the involvement of the ^5S or ^3F states of S^{2+} can result in the formation of S^+ in any of a significant number of states up to 33.1 eV in energy above the ground state of S. Of course, the neutral Ar will be in its ground electronic state, ^1S. The energy required to form Ar^+(^2P) from ground state Ar(^1S) is 15.8 eV. If solely the ^3P, ^1D or ^1S states of S^{2+} are involved in a SET reaction with Ar, Ar^+ can only be formed in its ground state, ^2P. If the ^5S state of S^{2+} is involved, Ar^+ could also be formed in its first excited state, ^2S, which lies at 29.2 eV above Ar(^1S). If S^{2+}(^3F) is involved, Ar^+ could be formed in any state with an energy of up to 38.5 eV above the ground state of Ar, of which there are approximately 30.

Table SI1 below lists the literature exoergicities of many of the large number of channels that are energetically available given the reactant and product electronic states we have discussed, with channels with exoergicities which fall in the reaction window highlighted in bold. Although many channels are nominally available, as shown in the article, the observed exothermicity spectrum corresponds nicely to reactions of the ^3P and ^1D states which we expect to dominate the beam.

Table SI1: Exoergicities of reaction pathways for the reaction S^{2+} + Ar → S^+ + Ar^+, calculated from literature values.[1,2] Ar is assumed to be in its ground state, ^1S. Highlighted in bold are the pathways with exoergicities between 4 eV and 7.4 eV, the energy range of the bulk of the experimental exoergicity signals.

Reactant (S^{2+}) states	**Product states**		**Total exoergicity**
S^{2+} state, relative to the ground state of S, (^3P)	Ar^+ state, relative to the ground state of Ar, (^1S)	S^+ state, relative to the ground state of S, (^3P)	Reactant states – total product states
^3P, 33.70 eV	^2P, 15.76 eV	^4S, 10.36 eV	7.58 eV
^3P, 33.70 eV	**^2P, 15.76 eV**	**^2D, 12.20 eV**	**5.74 eV**
^3P, 33.70 eV	**^2P, 15.76 eV**	**^2P, 13.40 eV**	**4.54 eV**
^3P, 33.70 eV	^2P, 15.76 eV	^4P, 20.20 eV	-2.27 eV
^3P, 33.70 eV	^2P, 15.76 eV	^2D, 22.50 eV	-4.56 eV
^3P, 33.70 eV	^2P, 15.76 eV	^2P, 23.45 eV	-5.51 eV
^3P, 33.70 eV	^2S, 29.24 eV	^4S, 10.36 eV	-5.90 eV
^3P, 33.70 eV	^2S, 29.24 eV	^2D, 12.20 eV	-7.74 eV
^3P, 33.70 eV	^2S, 29.24 eV	^2P, 13.40 eV	-8.94 eV
^3P, 33.70 eV	^2S, 29.24 eV	^4P, 20.20 eV	-15.75 eV
^3P, 33.70 eV	^2S, 29.24 eV	^2D, 22.50 eV	-18.04 eV
^3P, 33.70 eV	^2S, 29.24 eV	^2P, 23.45 eV	-18.99 eV
^3P, 33.70 eV	^4D, 32.17 eV	^4S, 10.36 eV	-8.83 eV
^3P, 33.70 eV	^4D, 32.17 eV	^2D, 12.20 eV	-10.67 eV
^3P, 33.70 eV	^4D, 32.17 eV	^2P, 13.40 eV	-11.87 eV
^3P, 33.70 eV	^4D, 32.17 eV	^4P, 20.20 eV	-18.67 eV
^3P, 33.70 eV	^4D, 32.17 eV	^2D, 22.50 eV	-20.97 eV

^{3}P, 33.70 eV	^{4}D, 32.17 eV	^{2}P, 23.45 eV	-21.92 eV
^{1}D, 35.10 eV	^{2}P, 15.76 eV	^{4}S, 10.36 eV	8.98 eV
^{1}D, 35.10 eV	**^{2}P, 15.76 eV**	**^{2}D, 12.20 eV**	**7.14 eV**
^{1}D, 35.10 eV	**^{2}P, 15.76 eV**	**^{2}P, 13.40 eV**	**5.94 eV**
^{1}D, 35.10 eV	^{2}P, 15.76 eV	^{4}P, 20.20 eV	-0.86 eV
^{1}D, 35.10 eV	^{2}P, 15.76 eV	^{2}D, 22.50 eV	-3.15 eV
^{1}D, 35.10 eV	^{2}P, 15.76 eV	^{2}P, 23.45 eV	-4.11 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{4}S, 10.36 eV	-4.50 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{2}D, 12.20 eV	-6.34 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{2}P, 13.40 eV	-7.54 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{4}P, 20.20 eV	-14.34 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{2}D, 22.50 eV	-16.63 eV
^{1}D, 35.10 eV	^{2}S, 29.24 eV	^{2}P, 23.45 eV	-17.59 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{4}S, 10.36 eV	-7.42 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{2}D, 12.20 eV	-9.27 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{2}P, 13.40 eV	-10.47 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{4}P, 20.20 eV	-17.27 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{2}D, 22.50 eV	-19.56 eV
^{1}D, 35.10 eV	^{4}D, 32.17 eV	^{2}P, 23.45 eV	-20.52 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{4}S, 10.36 eV	10.95 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{2}D, 12.20 eV	9.10 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{2}P, 13.40 eV	7.91 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{4}P, 20.20 eV	1.10 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{2}D, 22.50 eV	-1.19 eV
^{1}S, 37.07 eV	^{2}P, 15.76 eV	^{2}P, 23.45 eV	-2.15 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{4}S, 10.36 eV	-2.53 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{2}D, 12.20 eV	-4.38 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{2}P, 13.40 eV	-5.57 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{4}P, 20.20 eV	-12.38 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{2}D, 22.50 eV	-14.67 eV
^{1}S, 37.07 eV	^{2}S, 29.24 eV	^{2}P, 23.45 eV	-15.63 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{4}S, 10.36 eV	-5.46 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{2}D, 12.20 eV	-7.30 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{2}P, 13.40 eV	-8.50 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{4}P, 20.20 eV	-15.30 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{2}D, 22.50 eV	-17.60 eV
^{1}S, 37.07 eV	^{4}D, 32.17 eV	^{2}P, 23.45 eV	-18.55 eV
^{5}S, 40.97 eV	^{2}P, 15.76 eV	^{4}S, 10.36 eV	14.85 eV
^{5}S, 40.97 eV	^{2}P, 15.76 eV	^{2}D, 12.20 eV	13.01 eV
^{5}S, 40.97 eV	^{2}P, 15.76 eV	^{2}P, 13.40 eV	11.81 eV
^{5}S, 40.97 eV	**^{2}P, 15.76 eV**	**^{4}P, 20.20 eV**	**5.01 eV**
^{5}S, 40.97 eV	^{2}P, 15.76 eV	^{2}D, 22.50 eV	2.72 eV
^{5}S, 40.97 eV	^{2}P, 15.76 eV	^{2}P, 23.45 eV	1.76 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{4}S, 10.36 eV	1.37 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{2}D, 12.20 eV	-0.47 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{2}P, 13.40 eV	-1.67 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{4}P, 20.20 eV	-8.47 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{2}D, 22.50 eV	-10.76 eV
^{5}S, 40.97 eV	^{2}S, 29.24 eV	^{2}P, 23.45 eV	-11.72 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{4}S, 10.36 eV	-1.55 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{2}D, 12.20 eV	-3.40 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{2}P, 13.40 eV	-4.59 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{4}P, 20.20 eV	-11.40 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{2}D, 22.50 eV	-13.69 eV
^{5}S, 40.97 eV	^{4}D, 32.17 eV	^{2}P, 23.45 eV	-14.65 eV

^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{4}S, 10.36 eV	22.72 eV
^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{2}D, 12.20 eV	20.88 eV
^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{2}P, 13.40 eV	19.68 eV
^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{4}P, 20.20 eV	12.88 eV
^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{2}D, 22.50 eV	10.58 eV
^{3}F, 48.84 eV	^{2}P, 15.76 eV	^{2}P, 23.45 eV	9.63 eV
^{3}F, 48.84 eV	^{2}S, 29.24 eV	^{4}S, 10.36 eV	9.24 eV
^{3}F, 48.84 eV	**^{2}S, 29.24 eV**	**^{2}D, 12.20 eV**	**7.40 eV**
^{3}F, 48.84 eV	**^{2}S, 29.24 eV**	**^{2}P, 13.40 eV**	**6.20 eV**
^{3}F, 48.84 eV	^{2}S, 29.24 eV	^{4}P, 20.20 eV	-0.60 eV
^{3}F, 48.84 eV	^{2}S, 29.24 eV	^{2}D, 22.50 eV	-2.90 eV
^{3}F, 48.84 eV	^{2}S, 29.24 eV	^{2}P, 23.45 eV	-3.85 eV
^{3}F, 48.84 eV	**^{4}D, 32.17 eV**	**^{4}S, 10.36 eV**	**6.31 eV**
^{3}F, 48.84 eV	**^{4}D, 32.17 eV**	**^{2}D, 12.20 eV**	**4.47 eV**
^{3}F, 48.84 eV	^{4}D, 32.17 eV	^{2}P, 13.40 eV	3.27 eV
^{3}F, 48.84 eV	^{4}D, 32.17 eV	^{4}P, 20.20 eV	-3.53 eV
^{3}F, 48.84 eV	^{4}D, 32.17 eV	^{2}D, 22.50 eV	-5.82 eV
^{3}F, 48.84 eV	^{4}D, 32.17 eV	^{2}P, 23.45 eV	-6.78 eV

Scattering diagrams

To emphasize the weaker features of the scattering, the scattering diagrams in the paper are plotted using a logarithmic intensity scale. Such as scale, of course, makes the scattering look more angularly dispersed. To illustrate this point the figure below (Figure SI1) shows the same data as Figure 8 but on a linear intensity scale. Comparison of these two figures allows the reader to appreciate the directionality of the scattering.

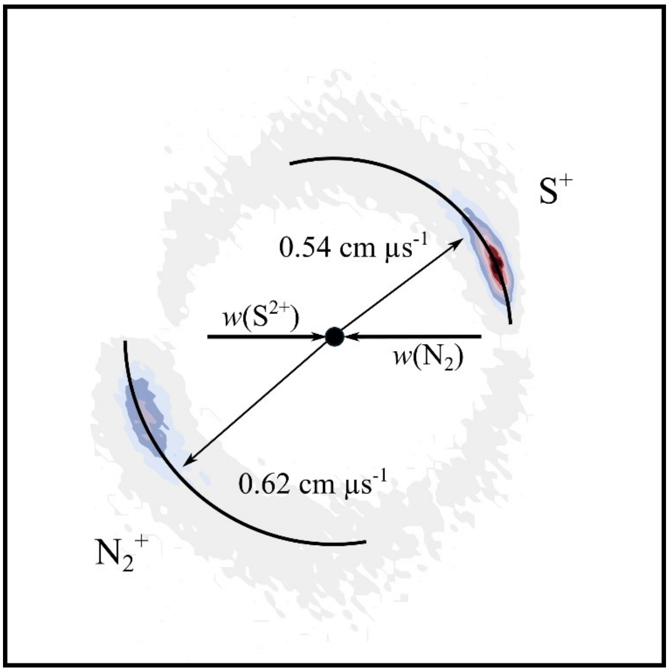

Figure SI1: CM scattering diagram for the reaction $S^{2+} + N_2 \rightarrow S^+ + N_2^+$ at a CM collision energy of 4.7 eV. The ion densities are represented with a linear scale, as opposed to a logarithmic scale (Figure 9). The black dot indicates the position of the CM. See text for details.

References

1 A. Kramida, Y. Ralchenko, J. Reader and NIST ASD Team, Eds., *NIST Atomic Spectra Database (version 5.6.1)*, National Institute of Standards and Technology, Gaithersburg, MD, 2020.

2 W. C. Martin, R. Zalubas and A. Musgrove, *J. Phys. Chem. Ref. Data*, 1990, **19**, 821–880.