

## IMAGING STUDIES OF S<sup>+</sup> FRAGMENTS FROM THE UV PHOTOLYSIS OF STATE-SELECTED H<sub>2</sub>S<sup>+</sup> CATIONS.

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Ion imaging methods have been used to study the dynamics of H<sub>2</sub>/D<sub>2</sub> elimination from H<sub>2</sub>S<sup>+</sup>/D<sub>2</sub>S<sup>+</sup> cations following photo-excitation to the A<sup>2</sup>A<sub>1</sub> state in the wavelength range 300 < λ < 360 nm.<sup>a</sup> Ground (X<sup>2</sup>B<sub>1</sub>) state parent ions were formed by 2+1 REMPI of H<sub>2</sub>S/D<sub>2</sub>S via the v=0 level of the <sup>1</sup>A<sub>2</sub>(...2b<sub>1</sub><sup>1</sup>4pb<sub>2</sub><sup>1</sup>) Rydberg state. This Rydberg state predissociates sufficiently slowly that the REMPI spectrum shows resolved rovibronic structure, thereby allowing full quantum state selectivity at this stage of the cation preparation process. Analysis of the S<sup>+</sup> ion images following one photon excitation of the resulting H<sub>2</sub>S<sup>+</sup>/D<sub>2</sub>S<sup>+</sup> cations reveals that these fragments are formed in their ground (<sup>4</sup>S) state, and that the H<sub>2</sub>/D<sub>2</sub> co-fragments are formed in rotational states with either odd or even J rotational quantum number - depending on the chosen REMPI preparation wavelength. This striking specificity for forming ortho- or para-H<sub>2</sub>/D<sub>2</sub> products can be traced to the state selectivity introduced in the REMPI preparation step. Two distinct fragmentation pathways for H<sub>2</sub>S<sup>+</sup>/D<sub>2</sub>S<sup>+</sup>(A) cations are identified. One involves non-adiabatic (Renner-Teller) coupling to the X state at near linear configurations and subsequent (spin-orbit induced) coupling to the repulsive <sup>4</sup>A<sub>2</sub> potential energy surface (PES) at smaller bond angles. This process operates throughout the photolysis wavelength range investigated and yields rotationally 'cool' and vibrationally 'cold' H<sub>2</sub> products. The second shows a long wavelength threshold λ~335 nm, and gradually becomes dominant as the photolysis wavelength is reduced. This mechanism involves vibronically facilitated non-adiabatic transfer from the A to the B<sup>2</sup>B<sub>2</sub> state, followed by spin-orbit induced transfer to the <sup>4</sup>A<sub>2</sub> PES; the resulting H<sub>2</sub> products carry higher levels of rotational and vibrational excitation.

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