IMAGING STUDIES OF S^+ FRAGMENTS FROM THE UV PHOTOLYSIS OF STATE-SELECTED H_2S^+ CATIONS.

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Ion imaging methods have been used to study the dynamics of H_2/D_2 elimination from H_2S^+/D_2S^+ cations following photo-excitation to the A^2A_1 state in the wavelength range $300< \lambda <360$ nm.[a] Ground (X^2B_1) state parent ions were formed by 2+1 REMPI of H_2S/D_2S via the v=0 level of the $^1A_2(...2b_1{}^1 4pb_2{}^1)$ 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^+ ion images following one photon excitation of the resulting H_2S^+/D_2S^+ cations reveals that these fragments are formed in their ground (^4S) state, and that the H_2/D_2 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_2/D_2 products can be traced to the state selectivity introduced in the REMPI preparation step. Two distinct fragmentation pathways for $H_2S^+/D_2S^+(A)$ 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 $^4A_2$ 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_2 products. The second shows a long wavelength threshold $\lambda\sim335$ 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^2B_2 state, followed by spin-orbit induced transfer to the $^4A_2$ PES; the resulting H_2 products carry higher levels of rotational and vibrational excitation.

[a] A.D. Webb, R.N. Dixon and M.N.R. Ashfold, *J. Chem. Phys.* **127**, 224307 (2007).