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Probing the Unusual Thresholds of AlH+/AlD+ formation by Molecular Dynamic Simulations on MRCI Potential Energy Surfaces NATHAN BREWER, Sigma Pi Sigma/SPS- Union University — In an experiment performed by P. Armentrout (Int. Rev. Phys. Chem. **1990**, 9, 115), the Al^+ cation was accelerated into the various isotopic combinations of H_2 to form AlH^+ and AlD^+. It was found that the product-forming reactions proceed very inefficiently. The experiments also showed a reduction of ∼29% in the threshold for the formation of AlD^+ from the HD reactant whereas all other AlH^+ and AlD^+ products formed at the same energetic threshold. Four previous theoretical attempts at capturing this unusual phenomenon have not been successful. The lowest energy singlet surfaces for the reaction of Al^+ with H_2 have been calculated at the multi-reference configuration interaction (MRCI) level of theory. The real/imaginary boundary of the symmetry-breaking b_2 vibrational mode was examined in three dimensions using Hessian matrices computed at a multi-configurational self-consistent field (MCSCF) level of theory. Molecular dynamic simulations numbering on the order of 10^7 were performed, sampling initial conditions reflective of the experiments. The simulations were run until they reached the location where the b_2 vibrational mode became unbound. A dissociation model was applied at these greatly compressed geometries to model the dissociation into AlH^+ and AlD^+ products.

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