POTENTIAL ENERGY SURFACES AND BRANCHING RATIO OF THE DISSOCIATIVE RECOMBINATION REACTION $HCNH^+ + e^-$: AN *AB INITIO* MOLECULAR ORBITAL STUDY

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Two dimensional potential energy surfaces for the dissociative recombination reaction, $HCNH^+ + e^- \rightarrow (HCNH)^* \rightarrow HCN/HNC + H$, have been calculated by the CASSCF-MRSDCI/cc-pVQZ *ab initio* molecular orbital method. Near the $HCNH^+$ ground state surface, which also represents the upper limit of the neutral HCNH Rydberg state surface, only two dissociative valence states of the HCNH are located: One is the $^2\Sigma^+$ state resulting in the H-C bond scission yielding HNC and the other the $^2\Sigma^+$ state resulting in the H-N bond scission yielding HCN.

The seam of intersection of these two surfaces almost bisects the zero-point vibrational wave function of the Rydberg-limit state of the neutral HCNH species, indicating that, while descending Rydberg ladder, transition to each dissociative surface occurs with almost equal probability. Thus, the branching ratio [HNC]/[HCN] is predicted to be nearly one or slightly more, explaining the thermochemically unrealistic interstellar [HNC]/[HCN] ratio of 4.4 observed toward L134N.