

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

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Two dimensional potential energy surfaces for the dissociative recombination reaction, $\text{HCNH}^+ + e^- \rightarrow (\text{HCNH})^* \rightarrow \text{HCN/HNC} + \text{H}$, 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 $[\text{HNC}]/[\text{HCN}]$ is predicted to be nearly one or slightly more, explaining the thermochemically unrealistic interstellar $[\text{HNC}]/[\text{HCN}]$ ratio of 4.4 observed toward L134N.