

Detection of Electronically Excited NH₂ product in the
Ultraviolet Photodissociation of Methylamine

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Methylamine (CH₃NH₂) which is the simplest ammonia (NH₃) derivative, has an electronic structure similar to NH₃. The non-adiabatic dynamics around the conical intersection of NH₃ has been interpreted as a nuclear motion that causes the branching to the electronically ground and excited products: NH₃ + hν → NH₂($\tilde{X}^2B_1$) + H / NH₂($\tilde{A}^2A_1$) + H. [1] Substitution of a H atom of NH₃ for a CH₃ group, allows the system to have the C-N and N-H bond cleavage channels. Although these two σ-bonds are known to dissociate following the UV absorption, the details of the dissociation mechanisms have not been clear. Particularly, the generation of the electronically excited NH₂ fragment is not established in both experimental and theoretical studies. [2]

Ion-imaging and dispersed fluorescence spectroscopy are applied for the photodissociation dynamics study of CH₃NH₂ in the photolysis wavelength range of 205-240 nm. The CH₃ product is found to populate a wide range of ro-vibrational states. The CH₃ fragment generated in the ν = 0 state shows the bimodal kinetic energy distribution. The internal energy analysis of the NH₂ counter-product indicates that a lower kinetic energy component, which was observed only with the CH₃(ν = 0) fragment, energetically matches the electronically excited $\tilde{A}^2A_1$ state. The dispersed fluorescence spectrum, whose band structure is assigned to the $\tilde{A}^2A_1 \rightarrow \tilde{X}^2B_1$ transition, provides evidence of the CH₃(ν = 0) + NH₂($\tilde{A}^2A_1$) pathway. [3] The branching mechanism of the product pathway is discussed in term of nuclear dynamics in the long-range region, [4] where the conical intersection between the excited and ground state potential energy surfaces can play a significant role.

References

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