SEMICLASSICAL STUDY OF THE PHOTODISSOCIATION DYNAMICS OF VIBRATIONALLY EXCITED $NH_3(\tilde{A})$ MOLECULES

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The photodissociation dynamics of ammonia upon excitation of the out-of-plane bending mode (mode ν_2 with n_2=0,..,6 quanta of vibration) on its $\tilde{A}$ electronic state is investigated by means of several semiclassical methods and compared to experiments. Five semiclassical methods are tested: one mean-field approach (the CSDM method), two surface-hopping methods (the FSTU and FSTU/SD methods) and two surface-hopping methods with zero-point energy preservation (the FSTU/SD/TRAPZ and FSTU/SD/mTRAPZ methods).[a] We found a qualitative difference between distributions obtained for $n_2 = 0$ and $n_2 > 1$ which is experimentally observed. Distributions obtained for $n_2 = 1$ present an intermediate behavior between distributions obtained for smaller and larger n_2 values. The dynamics is also found to be highly electronically nonadiabatic with all these methods. NH_2 internal energy distributions may have a negative energy tail when the zero-point energy (ZPE) conservation is not ensured throughout the dynamics. Unlike the original TRAPZ (TRAjectory Projection onto Zero-point energy orbits) method,[b] the mTRAPZ (modified TRAPZ) method does not lead to unphysical results and is much less time consuming. The effect of including ZPE corrections in semiclassical dynamics is also discussed in terms of agreement with experimental findings.

[a] A. W. Jasper, S. Nangia, C. Zhu and D. G. Truhlar, Acc. Chem. Res. **39**, 101 (2006); A. W. Jasper and D. G. Truhlar, J. Chem. Phys. **127**, 194306 (2007); D. Bonhommeau and D. G. Truhlar (in preparation)

[b] D. A. McCormack and K. F. Lim, Phys. Chem. Chem. Phys. **1**, 1 (1999)