ANHARMONIC QUASI-CLASSICAL BARRIER SAMPLINGS IN
TRAJECTORY CALCULATIONS AND THEIR INFLUENCE ON
THE COMPUTED PRODUCT ENERGY DISTRIBUTIONS

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Harmonic and anharmonic quasi-classical barrier samplings are used in classical
dynamics simulations to evaluate product energy distributions (PEDs). The results
obtained for the CH dissociation in the methanethiol cation (CH$_3$SH$^+$→CH$_2$SH$^+$ + H)
show that the PEDs are changed under inclusion of anharmonicity in the initial
conditions. Both the vibrational energy content at the transition state and the energy in
the transitional modes are important to explain the differences found in the PEDs.
Discrepancies between the PEDs obtained for trajectories initiated at the barrier and
those initiated at the reactant were found and explained on the basis of dynamical phase
space bottlenecks, which make the phase space density not uniform for $t \neq 0$. 