MOLECULAR DYNAMICS SIMULATIONS OF
THE HYDROGEN PEROXYL RADICAL

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ABSTRACT

The first study of this dissertation is focused on studies of the classical dynamics and associated rates of isomerization and dissociation of isolated HO₂. Comparisons are made between the three potential energy surfaces (PESs) used in these studies. The intramolecular vibrational energy redistribution (IVR) at energies above and below the threshold of isomerization is slow, especially for O–O stretch excitations, consistent with the regularity in the surfaces-of-section. The slow IVR rates lead to mode-specific effects that are prominent for isomerization and modest for unimolecular dissociation to H + O₂. Even with statistical distributions of initial energy, slow IVR rates result in bi-exponential decay for isomerization, with the slower rate correlated with slow IVR rates for O–O vibrational excitation. The calculated IVR results for all three PESs are reasonably well represented by an analytic, coupled three-mode energy transfer model.

The second study of this thesis is focused on the effects of pressure on the relaxation of the HO₂ embedded in a dense gas environment. A method of simulating the radical in an argon bath is proposed and validated. The time-dependent decay of vibrational energy is found to be bi-exponential for all of the simulated pressures. The relaxation rates at low pressures extrapolate poorly to the high-pressure results, with a turnover in the rate constants occurring at intermediate pressures. The effects of finite size on the simulation are investigated. Comparisons to studies with similar findings and additional considerations for understanding this behavior are discussed.