384i Use of Ab Initio Calculations to Estimate Global Warming Potentials for Hbrfc's: Atmospheric Lifetimes and Radiative Forcing Results

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Global warming potentials are one of the parameters used to evaluate the environmental performance of processes in life cycle assessments. Oftentimes, there is little information available in the standard databases of information about this measure or other environmental parameters. Ab initio calculations can provide accurate information for both atmospheric lifetimes and radiative forcing results used to compile global warming potentials. Computational chemistry methods are particularly well suited for investigating new chemical species before they are introduced into the environment. In this work, three (hydroflurorcarbons) HFC's and a series of hydrobromofluorocarbons (HBrFC's) are evaluated for both atmospheric lifetimes and radiative forcing results using ab initio calculations.

Geometry optimizations were done using the B3LYP method and a variety of basis sets to allow comparison to known molecular structures for reactants and products. Once high level geometries were obtained, a modified CBS composite energy method was applied to obtain heats of reaction and activation energies. The calculated results are compared to available data before being used to predict reaction energetics for species that have not been experimentally measured yet. Standard transition state theory was used to predict atmospheric reaction kinetics through the primary initial destruction reaction of hydrogen abstraction by hydroxyl radicals. This information yields atmospheric lifetimes and can be integrated into large scale atmospheric models to predict overall species distributions. Again, calculations were compared to the available experimental data before being used to predict reaction rates for other species.

Theoretical calculations to predict vibrational spectra were used to evaluate radiative forcing for the species and the results compared to prior work before being used for new species. The work here shows that ab initio calculations can be used to evaluate the environmental performance of many species, including those that are experimentally intractable to isolate and study.