Highly Accurate Thermochemical Properties of the Vinoxy Radical

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The vinoxy radical is an important intermediate in the combustion of hydrocarbon fuels, particularly the reaction of ethene with atomic oxygen [1]. In the past, experimental investigations of this radical have struggled to obtain reliable estimates of desired thermochemical quantities to within 10 kJ/mol. Previous computational studies applying the HEAT-345(Q) protocol obtain enthalpies of formation (0 K) for vinoxy and associated radicals [2] to ca. 2 kJ/mol, accounting for 26.2% of the Active Thermochemical Tables (ATcT, v1.124) provenance for this species [3]. Consequently, the ATcT uncertainty associated with this enthalpy of formation lingers near 0.6 kJ/mol. Here, we apply a version of extended HEAT treatments under development by the current authors to the vinoxy radical. These model chemistries [4] appear to elucidate bond energies of small molecules containing first- and second-row ($Z<10$) atoms to within 20 cm-1. The present study offers an opportunity to apply this approach to a molecule larger than those used to benchmark the original method. Newly developed composite techniques are critical components of this treatment, providing very accurate zero-point energies as well as vibrational wavefunctions with which to simulate vinoxy's photoionization spectrum.

References:

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