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, however, experimental investigations have faced considerable challenges in obtaining estimates of desired thermochemical quantities to within 10 kJ/mol. Computational studies thus account for the bulk of the Active Thermochemical Tables (ATcT) provenance for vinoxy, with the uncertainty of the ATcT enthalpy of formation lingering near 0.6 kJ/mol. In an attempt to reduce the uncertainty of these quantities, we apply an extended version of the HEAT model chemistry currently under development to the vinoxy radical and its associated cations. These treatments elucidate bond energies of small molecules containing first- and second-row atoms to within 20 cm^{-1}. Composite techniques provide very accurate zero-point energies for use in the thermochemical protocol and fundamental vibrational frequencies that are in excellent agreement with experiment. Anharmonic resonances are reanalyzed, suggesting an uncharacteristically complex CH stretching region. To compound matters, very little information is available concerning the photoionization spectrum of vinoxy, which is thought to undergo a large geometry change upon ionization. We report the adiabatic ionization energy for the vinoxy radical and a simulated photoionization spectrum generated from a harmonic autocorrelation function approach.