HIGHLY ACCURATE THERMOCHEMICAL PROPERTIES OF THE VINOXY RADICAL

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The vinoxy radical is an important intermediate in combustion processes, yet experimental investigations face considerable challenges obtaining accurate estimates of its thermochemical quantities. As a result, computational studies account for the bulk of the Active Thermochemical Tables (ATcT) provenance for vinoxy, with the uncertainty for the ATcT enthalpy of formation lingering near 0.6 kJ/mol. Due to the large geometry change upon ionization of vinoxy, it is difficult to establish the adiabatic ionization energy experimentally. The current adiabatic ionization energy quoted by ATcT via solely computational means is over 19 kJ/mol lower than experimental determinations, accompanied by an uncertainty of 1.5 kJ/mol.

In an attempt to reduce the ATcT uncertainties of these quantities, we apply an extended version of the HEAT model chemistry that is 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 recent experiments. Anharmonic resonances are reanalyzed, suggesting an uncharacteristically complex CH stretching region.