Accuracy of VPT2/CCSD(T) IR spectral estimation for broadened signals at STP conditions

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We present the accuracy of predicting excitation frequencies and absorption cross sections of gaseous IR spectra at room temperature and pressure via VPT2. Theorists have demonstrated that CCSD(T)/VPT2 treatments to estimate excitation energies are regularly accurate to within a few wavenumbers for single-reference molecules without pathological anharmonicity under experimental conditions. However, estimation of broadened signals, intended for use in the Earth's atmospheric temperature/pressure ranges, represents a different quantity altogether. Broadened signals reflect the superposition of Doppler/collisional effects coupled to transition dipole matrix elements for intensity. We also employ harmonic derivative-testing to identify Fermi and Dennison-Darling resonances. We compare CCSD(T)/VPT2 spectra of 10 molecules to NIST and HITRAN experimental databases. Our results benchmark the statistical error distributions of excitation frequencies and absorption cross sections. We similarly examine the statistical error distributions of using CCSD(T) diagonal couplings with MBPT(2) off-diagonal couplings as a reduced-cost scheme, as well as MBPT(2) for all vibrational couplings. All errors were found to be normally distributed