

Influence of Fourth-Order Vibrational Corrections on Semi-Experimental (r_e^{SE}) Structures of Linear Molecules

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Semi-experimental structures (r_e^{SE}) are derived from experimental ground-state rotational constants combined with theoretical vibrational corrections. They permit a meaningful comparison with equilibrium structures based on high-level *ab initio* calculations. Typically, the vibrational corrections are evaluated by Second-Order Vibrational Perturbation Theory (VPT2). The amount of error introduced by this approximation is generally thought to be small; however, it has not been thoroughly quantified. Herein, we assess the accuracy of the theoretical vibrational corrections by extending the treatment to Fourth-Order (VPT4) for a series of small, linear molecules. Typical corrections to bond distances are on the order of 10^{-5} Å—the largest being 0.0001 Å to the bond lengths of HNC. Treatment of vibrational effects beyond VPT2 will thus be important when one wishes to know bond distances confidently to four decimal places (10^{-4} Å). Certain molecules with shallow bending potentials, e.g., HOC^+ , are evidently not amenable to a VPT2 description and are unlikely to be improved by VPT4.