INFLUENCE OF FOURTH-ORDER VIBRATIONAL CORRECTIONS ON SEMI-EXPERIMENTAL STRUCTURES (r_e^{SE}) 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* computations. 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. When possible, comparisons to exact variational results are also made. Typical corrections to bond distances are on the order of 10^{-5} Å. Treatment of vibrational effects beyond VPT2 will thus be important when one wishes to know bond distances confidently to four decimal places. More substantial corrections (10^{-4} Å) are seen for HNC, CNCN, and NCCN. Certain molecules with shallow bending potentials, e.g., HOC^+, are not amenable to a VPT2 description and are not improved by VPT4.