Experimental accuracy from first principles: HF, CO and N_2 diatomics

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We have recently shown [1] that it is possible to achieve an accuracy of 0.10 cm^{-1} through state-of-the-art *ab initio* calculations for energy levels of seven water isotopologues up to 15000 cm^{-1} and J=25 and to produce *ab initio* water line intensities [2,3] with a typical accuracy of 1%, which supersedes the average experimental accuracy.

Extending this level of accuracy to other small (up to ~20 electrons), gas-phase molecules would constitute a significant breakthrough in theoretical spectroscopy. It would place calculated line positions considerably closer to typical experimental accuracy and would produce line intensities fully competitive with the very best experimental studies. We demonstrate the feasibility of this goal by presenting benchmark calculations for the HF, CO and N_2 diatomics.

While the solution of the nuclear-motion problem for closed-shell diatomics is straightforward, their electronic structure treatment is appreciably but not overwhelmingly simpler than that of polyatomic molecules with a similar number of electrons. As a result errors in calculated energy levels and intensities of diatomics are fully representative of the level of accuracy also achievable for polyatomic molecules, albeit at an increased computational investment (mainly due to the larger number of *ab initio* points necessary and to the complexity of the many-body nuclear-motion problem). HF, CO and N_2 are prototypical molecules with single, double and triple bonds respectively. Both CO and N_2 are known to have a complicated, highly multi-reference electronic structure. We report *ab initio* energy levels up to 25,000 cm^{-1} for all three molecules which reproduce measured values with a root-mean-square deviation (RMSD) of better than 0.1 cm^{-1}; rotationally-excited states with J=40 for HF and J=100 for CO are also reproduced with similar accuracy. For comparison, the previous best *ab initio* calculations for HF [4] and CO [5] have RMSD of 1.3 cm^{-1} and 6.0 cm^{-1} respectively. For HF we also report energy levels all the way up to dissociation (~49 400 cm^{-1}) with near-dissociation errors of only a few cm^{-1}.

For CO we also present computed line intensities for various isotopologues which deviate by less than 1% with respect to recent, very accurate experimental data [6,7].

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