TOWARDS EXPERIMENTAL ACCURACY FROM THE FIRST PRINCIPLES

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Producing *ab initio* ro-vibrational energy levels of small, gas-phase molecules with an accuracy of 0.10 cm^{-1} would constitute a significant step forward in theoretical spectroscopy and would place calculated line positions considerably closer to typical experimental accuracy. Such an accuracy has been recently achieved[a] for the H_3^+ molecular ion for line positions up to 17 000 cm^{-1}. However, since H_3^+ is a two-electron system, the electronic structure methods used in this study are not applicable to larger molecules.

A major breakthrough was reported in ref.[b], where an accuracy of 0.10 cm^{-1} was achieved *ab initio* for seven water isotopologues. Calculated vibrational and rotational energy levels up to 15 000 cm^{-1} and $J = 25$ resulted in a standard deviation of 0.08 cm^{-1} with respect to accurate reference data. As far as line intensities are concerned, we have already achieved[c] for water a typical accuracy of 1% which supersedes average experimental accuracy.

Our results are being actively extended along two major directions. First, there are clear indications that our results for water can be improved to an accuracy of the order of 0.01 cm^{-1} by further, detailed *ab initio* studies. Such level of accuracy would already be competitive with experimental results in some situations. A second, major, direction of study is the extension of such a 0.1 cm^{-1} accuracy to molecules containg more electrons or more than one non-hydrogen atom, or both. As examples of such developments we will present new results for CO, HCN and H_2S, as well as preliminary results for NH_3 and CH_4.

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[a] O.L. Polyansky, A. Alijah, N.F. Zobov, I.I. Mizus, R. Ovsyannikov, J. Tennyson, L. Lodi, T. Szidarovszky and A.G. Csaszar, *Phil. Trans. Royal Soc. London A*, **370**, 5014-5027 (2012).

[b] O.L. Polyansky, R.I. Ovsyannikov, A.A. Kyuberis, L. Lodi, J. Tennyson and N.F. Zobov, *J. Phys. Chem. A*, (in press).

[c] L. Lodi, J. Tennyson and O.L. Polyansky, *J. Chem. Phys.* **135**, 034113 (2011).