MARVEL: Measured Active Rotational-Vibrational Energy Levels

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Information systems containing a large amount of spectroscopic and thermochemical data have a special relevance for scientific and engineering modeling efforts, including those of the atmosphere of earth.

An algorithm, based principally on earlier work of Flaud and co-workers, is proposed that inverts the information contained in uniquely assigned experimental rotational-vibrational transitions in order to obtain measured active rotational-vibrational energy levels (MARVEL). The procedure starts with collecting, critically evaluating, selecting, and compiling all available measured transitions, including assignments and uncertainties, into a single database. Then, components of spectroscopic networks (SN) are determined which contain all interconnecting rotational-vibrational energy levels supported by the grand database of the selected transitions. Adjustment of the uncertainties of the lines is performed next, with the help of a robust reweighting strategy, until a self-consistent set of lines and related uncertainties is determined. Inversion of the transitions through a weighted least-squares-type procedure results in MARVEL energy levels and associated uncertainties.

The MARVEL technique has been used to handle and validate measured transitions of the following isotopologues of the water molecule: $H_2{}^{16}O$, $H_2{}^{17}O$, $H_2{}^{18}O$, $HD^{16}O$, $HD^{17}O$, and $HD^{18}O$. From these water isotopologues, the $HD^{16}O$ has the second largest database containing about 55,000 transitions and 9,000 energy levels. To handle much larger datasets, like the database of $H_2{}^{16}O$ involving nearly 200,000 measured transitions (of which almost 100,000 are unique), required us to improve all of the algorithms the original MARVEL code employed.

Owing to the algorithmic improvements, the present version of the MARVEL code is much faster and more reliable than the original one. Complete reatment of large datasets (for example, that of $H_2{}^{16}O$) takes just a fraction of a second.

The same approach can be used not only for spectroscopy but also for thermochemistry when improved estimates of enthalpies of formation can be determined.