Networks in thermochemistry and spectroscopy

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Following the successes of Chemical Graph Theory (CGT), complex graphs (network) seem to gain new roles in chemistry via their ability to enhance the treatment of large databases.

The MARVEL algorithm and code we developed [1] is based on the theory of spectroscopic networks [2] and combines it with a weighted linear least-squares protocol for data inversion. MARVEL, standing for *M*easured *A*ctive *R*otational-*V*ibrational *E*nergy *L*evels, can be employed to determine experimental energy levels and their uncertainties from a database of experimentally measured and assigned transitions coming from high-resolution spectroscopy. Algorithmic improvements characterizing the second generation of the MARVEL code [3] make it possible to invert the information contained in hundreds of thousands of transitions. Some of these algorithms are explained during the talk. The most important application of MARVEL has been the determination of all the known experimental energy levels of all the major isotopologues of the water molecule.

Similar in its design to MARVEL, we also developed a thermochemical protocol and code termed NEAT [4]. Its name refers to the fact that with NEAT our aim is to move from a *N*etwork of computed reaction *E*nthalpies toward *A*tom-based *T*hermochemistry. Another aim of NEAT is to tighten the uncertainties of first-principles enthalpies of formation via forming a large number of cycles in a thermochemical network. The largest network we use contains hundreds of ab initio reaction enthalpies and results in dependable enthalpies of formation for tens of species. The NEAT enthalpies of formation are very similar to thos obtained from the ATcT approach.

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