Spectroscopic networks: small molecules as complex systems

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Several research fields in chemistry, including high-resolution molecular spectroscopy as well as thermochemistry and reaction kinetics, handle an extreme amount of data, most of which is deposited in information systems. In all these areas there is a strong ongoing activity to gather new data (preferentially via specifically designed new experiments yielding the most useful information), critically evaluate and validate them (with respect to all the available data), improve the overall quality of the resulting information system (to always provide the best existing data for, for example, engineering and scientific applications), and thus turn information into knowledge in the most efficient way. To ease these activities use of the language and the algorithms provided by network (graph) theory is recommended.

For individual molecules quantum mechanics (QM) offers a simple, natural and elegant way to build large-scale (complex) networks: quantized energy levels are the nodes, allowed transitions among the levels are the links, and transition intensities supply the weights. QM networks are characterized experimentally via spectroscopy; thus, realizations of QM networks are called spectroscopic networks (SN). As demonstrated most clearly for the SN of $H_2{}^{16}O$, involving the largest experimental SN studied containing some 200 000 transition entries and about 20 000 rovibrational energy levels and the largest *ab initio* SN containing 200 000 nodes and half a billion of links, both the measured and certain first-principles computed one-photon absorption and emission networks appear to have definitely top heavy and likely scale-free degree distributions, with a scaling parameter slightly above 2. The proposed novel view of high-resolution spectroscopy and the observed scaling of the degree distribution of SNs have important practical consequences: appearance of hubs among the energy levels, arguments about assortativity, robustness, error tolerance, and an "ultra-small-world" property of SNs. A data reduction facility via a minimum-weight spanning tree approach, which can assist high-resolution spectroscopists to improve the efficiency of the assignment of measured spectra, is a consequence of this view.

Inversion of the measured transitions to yield experimental energy levels, based on the concept of SNs, is called MARVEL (*m*easured *a*ctive *r*otational-*v*ibrational *e*nergy *l*evels). Efficient algorithms developed allow to carry out a least-squares analysis of large SNs within a fraction of a second. MARVEL has been used to analyse high-resolution spectroscopic data for $^{12}C_2$, nine isotopologues of water, for three isotopologues of H_3^+, for $^{14}NH_3$, and for parent ketene. The special role of results from "fourth-age" quantum chemical techniques during the spectroscopic analysis is emphasized.