AN OPTIMAL STRATEGY FOR REPRESENTING EXTENSIVE DIATOMIC MOLECULE DATA SETS

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A longstanding problem in diatomic molecule spectroscopy has been how to provide optimal compact, accurate and comprehensive representations of very extensive data sets. While widely used since the earliest days of quantum mechanics, the traditional polynomials in $(v + \frac{1}{2})$ for representing vibrational energies and rotational constants have significant drawbacks, in that they extrapolate quite unreliable, and for sufficiently extensive data sets, separate polynomials have to be used for different v ranges. An alternative approach of using "top-down" *near-dissociation expansions* which incorporate the correct theoretically-known limiting functional behaviour near dissociation has been advocated and successfully applied to a number of systems.[a] However, when insufficient care is applied they too can sometimes misbehave in the extrapolation region, especially when the numbers of empirical expansion parameters become relatively large. More seriously, when large numbers of expansion parameters are required it becomes increasingly difficult to determine adequate initial trial parameters for starting the requisite non-linear least-squares fits. A third approach, introduced by Tellinghuisen and co-workers,[b,c] is to use "mixed" representations which are essentially pure $(v + \frac{1}{2})$ polynomials at low–v, but smoothly convert to near-dissociation expansions for high–v. This paper will critically compare these three approaches and attempt to delineate when one or another would most effectively satisfy the above requirements for an optimal method of data representation.

[a] J.W. Tromp and R.J. Le Roy, *J. Mol. Spectrosc.* **109**, 352 (1985).
[b] J. Tellinghuisen and J.G. Ashmore, *Chem. Phys. Lett.* **102**, 10 (1983).
[c] J. Tellinghuisen, *J. Chem. Phys.* **118**, 3532 (2003).