DIRECT FITTING OF SPECTROSCOPIC DATA TO MODEL POTENTIALS: PROBLEMS, PROMISE, AND ILLUS-TRATIVE APPLICATIONS

JENNING Y. SETO and ROBERT J. LE ROY, *Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*.

Historically, spectroscopists have usually analyzed their data by fitting to level energy models expressed as analytic functions (usually polynomials) of the vibrational and rotational quantum numbers. However, this approach tends to require large numbers of expansion parameters, only a few of which have independent physical significance, and predictions beyond the range of the input data often have limited reliability. A promising method of addressing these problems is to directly fit the spectroscopic data to analytical potentials (and Born-Oppenheimer breakdown correction functions) based on the natural physical behaviour of the molecule of interest, and a number of successful applications of this approach have been reported. However, the widespread adoption of this approach has been hindered by a number of practical computational problems, including difficulties in automatically generating the realistic trial eigenvalues for arbitrary observed levels required by the Schrödinger-solver subroutine, obtaining plausible initial trial potential parameters, and problems with the extrapolation properties of the resulting potentials (and Born-Oppenheimer breakdown correction) functions. Our recent progress in addressing these problems and providing a general, robust and "easy"-to-use computer program for analysing data in this way will be presented and illustrated by applications to a number of systems.