TREATING Λ-DOUBLING IN PARAMETER-FIT AND DIRECT-POTENTIAL-FIT DATA ANALYSES

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

Most conventional treatments of Λ-doubling level shifts in diatomic molecule data analysis involve simply fitting to empirical parameters $q_B(v)$, $q_D(v)$, ... etc., for each vibrational level of each isotopomer of the given molecular state (sometimes representing their vibrational dependence as Dunham-type power series in $(v + \frac{1}{2})$), usually without concern regarding whether it is the e or f sub-levels which are affected by the perturbation, or for any implicit relationships between the $q_B(v)$ and higher-order parameters. We show that in parameter-fit analyses, explicitly treating the appropriate set of sub-levels as being unperturbed yields more successful systematic fits to data involving Λ-doubling, which in turn yields both a better description of the "mechanical behaviour" of such systems and a cleaner delineation of the perturbation effects. This capability is being implemented in the publicly-available general-purpose data analysis program DParFit 3.0 (http://leroy.uwaterloo.ca). The same type of discrimination has been applied in direct-potential-fit data analyses, in which direct fits of simulated spectra generated by exact quantum mechanical solution of the radial Schrödinger equation to experimental data are used to determine accurate analytic functions for the relevant potential energy curves. It is shown that in this case the effect of Λ-doubling may be represented by a radial strength function incorporated into the effective potential energy function for the system, but only affecting levels of the appropriate (e or f) symmetry. The utility of these procedures is demonstrated by illustrative applications.