SPLINE FITTING OF TERM ENERGIES AND ROTATIONAL CONSTANTS

D. L. HUESTIS, SRI International, Molecular Physics Laboratory, Menlo Park, CA 94025.

We will describe recent developments and applications of using spline functions to fit vibrational term energies and rotational constants from the potential minimum to the dissociation limit without a switching function.

For a number of electronic states of diatomic molecules we have experimental values for the vibrational term energies and rotational constants from \( v = 0 \) to just below the dissociation limit. For low \( v \) the Dunham expansion is immediately interpretable as describing the potential energy curve near its minimum. For high \( v \) a near-dissociation (ND) representation similarly corresponds to the \( 1/R \) power series expansion of the long range potential.

However, accurate construction of potential curves by the RKR method requires continuous differentiable functional representations of \( G_v \) and \( B_v \) over the whole range of vibrational levels. One approach is to combine the Dunham and ND functions using a switching function for intermediate \( v \).

Here we propose an alternative approach of linear least-squares fitting (LLSQF) of \( G_v \) and \( B_v \) (or transformed versions) using cubic splines. Because each cubic-spline basis function represents only a narrow range of \( v \) values, the spline fit does not suffer from the limited convergence radii of the Dunham and ND expansions. In addition, LLSQF makes it easier to propagate uncertainties in \( G_v \) and \( B_v \) into statistical confidence limits for the \( f_v \) and \( g_v \) RKR integrals.

Results will be presented for potential curves of \( \text{O}_2 \) and \( \text{I}_2 \).