SPLINE FITTING OF TERM ENERGIES AND ROTATIONAL CONSTANTS

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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 O_2 and I_2.