At last year’s ISMS meeting, Zaleski et al. reported new broadband MW spectroscopy measurements of pure rotational transitions in the $v = 0 – 6$ levels of the $^2\Pi_{1/2}$ ground electronic state of PbI.\(^a\) The analysis presented at that time was a conventional $v$-level by $v$-level ‘band-constant’ analysis performed using the PGopher program.\(^b\) That level-by-level PGopher analysis yielded values of $B_v$, $D_v$ and five spin-splitting parameters for each vibrational level of each isotopologue. Ignoring the spin-splitting information, the $B_v$ and $D_v$ values were used to generate a set of synthetic pure $R(0)$ transitions for each level that were taken to represent the “mechanical” information about the molecule contained in these spectra. A standard direct-potential-fit (DPF) analysis\(^c\) was then used to fit these data to an “Expanded Morse Oscillator” (EMO) potential function form. The well-depth parameter $D_e$ was fixed at the literature value, while values of the equilibrium distance $r_e$ and three EMO exponent-coefficient expansion ‘potential shape’ parameters are determined from the fits. The best fits to the data yield potentials whose fundamental vibrational spacings are in excellent agreement with experiment\(^d\) together with reliable predictions for the first five overtone energies.


\(^b\) PGopher - a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, http://pgopher.chm.bris.ac.uk
