IMPROVED PARAMETERIZATION FOR DIATOMIC BORN-OPPENHEIMER BREAKDOWN EFFECTS, AND A NEW COMBINED-ISOTOPES ANALYSIS FOR HD AND DF

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

Although the Ross et al.\textsuperscript{a}-Bunker\textsuperscript{b}-Watson\textsuperscript{c} expression for the vibration-rotation levels of isotopomers-\(Q\) of diatomic molecule \(A-B\),

\[ E^Q(v, J) = \sum_{\ell,m} \frac{U_{\ell,m}}{(\ell+1)^2} \left( 1 + \frac{n \Delta_{\ell,m}^A + m \Delta_{\ell,m}^B}{n-m} \right) (v+1/2)^{\ell} [J(J+1)]^m, \]

is fairly widely used, it has a number of deficiencies. In particular: (i) it is not clear how to treat the \((\ell, m) = (0, 0)\) term, (ii) the \(U_{\ell,m}\) constants have inconveniently varying units depending on fractional powers of the mass, (iii) fits to data for only two isotomers cannot yield "true" mass-independent \(U_{\ell,m}\) values, (iv) for non-hydrides, the magnitudes of the \(U_{\ell,m}\) constants are not even qualitatively similar to those of the analogous familiar Dunham \(Y_{\ell,m}\) constants, and (v) direct fits to this expression are impossible, so non-linear fits or indirect methods must be used to determine the \(\Delta_{\ell,m}^A\) values and their uncertainties. Moreover, this formulation is incompatible with the use of non-Dunham expressions (such as near-dissociation expansions) for the vibrational energies and rotational and centrifugal distortion constants. The present paper presents an alternate description of the Born-Oppenheimer and JWKB breakdown corrections which resolves all of these difficulties, and illustrates its use by a combined-isotopes analysis of the best available microwave, infrared and electronic data for the ground electronic states of HF and DF.

\textsuperscript{b}P.R. Bunker, J. Mol. Spectrosc. 68, 367 (1977)
\textsuperscript{c}J.K.G. Watson J. Mol. Spectrosc. 68, 367 (1977)