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

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Although the Ross *et al.*[a]-Bunker[b]-Watson[c] expression for the vibration-rotation levels of isotopomers-α of diatomic molecule A–B, $E^{\alpha}(v,J) = \sum_{l,m} \frac{U_{l,m}}{(\mu)^{l+m/2}} \left(1+\frac{m_e}{m_A}\Delta^A_{l,m}+\frac{m_e}{m_B}\Delta^B_{l,m}\right)(v+1/2)^l\,[J(J+1)]^m$, is fairly widely used, it has a number of deficiencies. In particular: (i) it is not clear how to treat the $(l,m)=(0,0)$ term, (ii) the $U_{l,m}$ 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 $U_{l,m}$ values, (iv) for non-hydrides, the magnitudes of the $U_{l,m}$ constants are not even qualitatively similar to those of the analogous familiar Dunham $Y_{l,m}$ constants, and (v) direct fits to this expression are impossible, so non-linear fits or indirect methods must be used to determine the $\Delta^a_{l,m}$ 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.

[a] A.H.M. Ross, R.S. Eng and H. Kildal, *Opt. Commun.* **12**, 433 (1974)
[b] P.R. Bunker, *J. Mol. Spectrosc.* **68**, 367 (1977)
[c] J.K.G. Watson *J. Mol. Spectrosc.* **68**, 367 (1977)