

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 isotomers- α of diatomic molecule $A-B$, $E^\alpha(v, J) = \sum_{l,m} \frac{U_{l,m}^\alpha}{(\mu_B)^{l+m-2}} (1 + \frac{m^2}{m_A^2} \Delta_{l,m}^A + \frac{m^2}{m_B^2} \Delta_{l,m}^B) (v+1/2)^l [J(J+1)]^m$, 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 $\Delta_{l,m}^a$ 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.

^aA.H.M. Ross, R.S. Eng and H. Kildal, *Opt. Commun.* **12**, 433 (1974)

^bP.R. Bunker, *J. Mol. Spectrosc.* **68**, 367 (1977)

^cJ.K.G. Watson *J. Mol. Spectrosc.* **68**, 367 (1977)