ACCURATE MOLECULAR CONSTANTS, POTENTIAL CURVE AND BORN-OPPENHEIMER BREAKDOWN CORRECTION FUNCTIONS FOR $X\,^1\Sigma_g^+$ MgH and MgD

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New high resolution Fourier Transform spectra of the 0–3, 0–4, 1–3, 1–4 and 1–5 bands of the $B'\,^2\Sigma^+ - X\,^2\Sigma^+$ transition of MgH, together with lines from sunspot spectra coupling B'–state levels $v' = 0$ & 1 to X–state levels $v'' = 3 - 8$, combined with older $B' - X$ band data[a] involving $v''(X) = 3 - 9$ and $v'(B') = 0 - 9$ and ground-state 2–1 and 1–0 infrared data, yield a description of the ground state for $v'' = 0 - 2$ and $v'' = 3 - 9$. The $v'' = 2 - 3$ gap was bridged using transitions from the 1–2 and 1–3 bands of the $A\,^2\Pi - X\,^2\Sigma^+$ spectrum. In order to avoid complications due to perturbations in the excited state, all of these electronic band data were re-arranged and treated as fluorescence series into the ground state. The resulting data set consisted of a total of 4140 transitions for six isotopomers of MgH and MgD.

We have performed two types of combined isotopomer analyses of these data. (i) A fit to empirical Dunham-type expansions which included hydrogenic Born-Oppenheimer breakdown correction terms required 54 expansion parameters, plus the 701 "fluorescence series" origins. However, the resulting empirical centrifugal distortion constants will be unreliable for extrapolation to J values significantly higher than those included in the data set. (ii) An equally good fit to an analytic model potential energy function plus adiabatic and non-adiabatic radial Born-Oppenheimer breakdown correction functions required only 21 potential and correction-function parameters, plus the 701 "fluorescence series" origins. The resulting potential function has the MLJ form,[b] and was constrained to have the correct C_6/R^6 long-range behaviour, so it should prove highly reliable for extrapolations in v or J. The parameter-fit and potential-fit computer programs used for this analysis were DSParFit and DSPotFit.[c]

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[a] W.J. Balfour and H.M. Cartwright, *Can.J.Phys.* **54**, 1898 (1976); W.J. Balfour and B. Lindgren, *Can.J.Phys.* **56**, 767 (1978).

[b] P.H. Hagigeorgiou and R.J. Le Roy, *J. Chem. Phys.* **112**, 3949 (2000).

[c] Program source code and manuals available through the "Computer Programs" link on the www site http://leroy.uwaterloo.ca.