THE UNIVERSAL POTENTIAL ENERGY CURVE: A VALENCE STATE APPROACH

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A universal potential energy function, capable of predicting Rydberg-Klein-Rees (RKR) \(^i\) "experimental" curves and the higher spectroscopic constants, \(\alpha_e\) and \(\bar{\alpha}_e x_e\) for diatomic molecules to better accuracy than previously known, has been developed. The function was formulated to fulfil the general criteria for potential energy curves as stated by Varshni\(^ii\) and is semiempirical in nature.

The Valence State (VS) of Atoms-in-Molecules (AIM) as introduced by Van Vleck and Mulliken and later extended by Ruedenberg\(^iii\) has been applied for the first time to the universal potential energy curve problem. The Valence State Atoms-in-Molecule (VSAM) model is used to develop Valence State potential energy (VS-PE) curves, which "transitions" around the minimum, in a "soft" Coulson-Fischer\(^iv\) manner, to Valence State-Morse (VSM) ground state curves generating Universal Ionic-Covalent (UIC) curves. The representation of nearly one hundred ground, excited and ionic molecular states of several bond types is presented and the successes of the model highlighted.

Non-linear universal scaling techniques have been used to reduce RKR curves of nearly fifty molecule, of ionic and covalent nature, into essentially a single curve. This UIC scaling technique is also novel and incorporates the transition from VS atoms to the ground state. The different nature of the AIM, as an atom in a molecule (AIM) and a "pure" non-bonded atom, has been suitably represented. Reference of the AIM to the VS is a necessary criterion for universality.

\(^i\) (a) R. Rydberg, Z. Physik 73, 376 (1931); ibid. 80, 514 (1933); (b) O. Klein, Z. Physik 76, 221 (1932); (c) A.L.G. Rees, Proc. Phys. Soc. (London) 59, 998 (1947)
\(^ii\) Y.P. Varshni, Rev. Mod. Phys. 29, 664 (1957)
\(^iii\) K. Ruedenberg, Rev. Mod. Phys. 34, 326 (1962)
\(^iv\) C.A. Coulson and I.H. Fischer, Philos. Mag. 40, 386, (1949)