ABSTRACT

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, α_e and $\tilde{\upsilon}_e x_e$ 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.

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[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)