

NEW WAYS OF TREATING DATA FOR DIATOMIC MOLECULE 'SHELF' AND DOUBLE-MINIMUM STATES

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Electronic states whose potential energy functions have 'shelf' or double-minimum shapes have always presented special challenges because, as functions of vibrational quantum number, the vibrational energies/spacings and inertial rotational constants either have an abrupt change of character with discontinuous slope, or past a given point, become completely chaotic. The present work shows that a 'traditional' methodology developed for deep 'regular' single-well potentials can also provide accurate 'parameter-fit' descriptions of the v -dependence of the vibrational energies and rotational constants of shelf-state potentials that allow a conventional RKR calculation of their Potential energy functions. It is also shown that a merging of Pashov's uniquely flexible 'spline point-wise' potential function representation with Le Roy's 'Morse/Long-Range' (MLR) analytic functional form which automatically incorporates the correct theoretically known long-range form, yields an analytic function that incorporates most of the advantages of both approaches. An illustrative application of this method to data to a double-minimum state of Na_2 will be described.