

FORM OF THE LEADING DEVIATION FROM THE LIMITING NEAR-DISSOCIATION BEHAVIOUR OF DI-ATOMIC MOLECULES

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It is well known that the limiting near-dissociation behaviour of the vibrational level energies and other properties of diatomic molecules are determined by the nature of the asymptotically-dominant attractive inverse-power term in the intermolecular potential energy function, $V(R) \simeq \mathcal{D} - C_n/R^n$. For the vibrational energies, the associated eigenvalue expression is $G(v) = \mathcal{D} - X_0(n) (v_D - v)^{2n/(n-2)}$, where v_D is the effective (noninteger) vibrational index at dissociation, $X_0(n) = \overline{X}_0(n)/[\mu^n (C_n)^2]^{1/(n-2)}$ and $\overline{X}_0(n)$ is a known numerical constant. Fits to this expression have been used to determine accurate dissociation energies and v_D values and some of the best experimental estimates of long-range potential C_n constants. However, the observed levels rarely all lie sufficiently close to dissociation that this limiting level energy expression is completely appropriate. At the same time, it is expected that the leading correction to this limiting expression will be defined by the nature of the second longest-range inverse-power term in the long-range potential $V(R) = \mathcal{D} - C_n/R^n - C_m/R^m - \dots$, and it seems reasonable to expect that taking account of this leading correction term will allow better vibrational extrapolations and better experimental determinations of long-range potential constants. This paper will present and illustrate the use of explicit expressions for the leading correction to the limiting near-dissociation behaviour of the vibrational energies for a variety of cases.