

Dissociation energy of diatomic molecules

SARVPREET KAUR and C G MAHAJAN

Centre of Advanced Study in Physics, Panjab University, Chandigarh 160 014, India

E-mail: spectphys@ch1.vsnl.net.in

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Abstract. The dissociation energy of twelve diatomic molecules has been determined by fitting four-parameter potential function $U(r) = D_e \{ [1 - \exp\{-b(r - r_e)\}] / [1 - C \exp\{-b(r - r_e)\}] \}^2$ to the true Rydberg–Klein–Rees (RKR) curves for their fifteen electronic states using the mean square deviation as the criterion for the selection of the best fit. Average deviation of D_e has been found to be 2.7% as compared to 20.5% obtained with Lippincott's potential function for these molecules. In addition the anharmonicity constant $\omega_e x_e$ has also been calculated for the same electronic states yielding average mean deviation 8.9%.

Keywords. Dissociation energy; four-parameter potential; anharmonicity constant.

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1. Introduction

The spectroscopic data for most of the diatomic molecules is available for vibrational levels which are considerably below the dissociation limit. So different extrapolation methods have been employed to find the dissociation energy of these molecules and Birge–Sponer [1] approach is most commonly used for this purpose. Obviously, the results inherently suffer from an uncertainty determined by the extrapolation gap and the method of extrapolation. In addition, it has long been known [2] that vibrational energies near the dissociation limit and hence the vibrational spacings depend on the functional form of the long range potential. This, in turn, leads to a marked deviation of graphical extrapolation from the accurate estimate of the dissociation limit. Using asymptotic approximation for long range potentials of the form

$$V(r) = D_e - \sum_n \frac{C_n}{r^n}, \quad (1)$$

where D_e is the dissociation limit of the potential and C_n is given by

$$E(v) = D_e - \frac{C_n}{(r_{\max}(v))^2}. \quad (2)$$

LeRoy and co-workers [2–4] have developed WKB based extrapolation technique to estimate the dissociation limits. Their near-dissociation expansion (NDE) formalism has led to results far better than the Birge–Sponer extrapolation method. It may, however,