Dissociation energy of diatomic molecules

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Abstract. The dissociation energy of twelve diatomic molecules has been determined by fitting four-parameter potential function \( U(r) = D_e \left[ \frac{1 - \exp \left( -b(r - r_e) \right)}{1 - C \exp \left( -b(r - r_e) \right)} \right]^2 \) 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 \( \omega_x \) 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

\[
V(r) = D_e - \sum_n \frac{C_n}{r^n},
\]

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

\[
E(v) = D_e - \frac{C_n}{(r_{\text{max}}(v))^2}.
\]

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,
be pointed out that a proper RKR analysis yields a much more accurate estimate of \( D_e \) [5].

In 1990, Wei Hua introduced a four-parameter (FP) potential function [6],

\[
U(r) = D_e \left[ \frac{1 - \exp\{-b(r - r_e)\}}{1 - C \exp\{-b(r - r_e)\}} \right]^2,
\]

where \( b = (1 - C)a \), and \( C \) is an adjustable parameter having \(|C| < 1\) with \( a = \sqrt{k_e/2D_e} \).

The FP potential fits very closely to the RKR curves compared to Morse and other analytical functions [6], when the potential domain extends to near dissociation limit. It is, therefore, natural to expect that FP potential would predict the dissociation limit precisely. We have made an attempt to investigate this aspect of the FP potential and the results constitute the content of this communication. Wei Hua considered fifteen electronic states of twelve molecules to examine his FP potential and the same electronic states have been used in the present studies as the spectroscopic constants, the RKR potential curves and the dissociation energies are known very accurately for these states. The molecular constants and respective dissociation energies are given in table 1.

### 2. Estimation of the dissociation energy

Because of the anharmonicity the molecules in the highly excited vibrational levels spend most of their time in the neighborhood of outer turning points. Therefore, the vibrational spacings [2], rotational constants [7] and other properties [8] of the diatomic molecules near the dissociation limit, are explained mainly by the outer limb of the potential curve.
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Accordingly we have used the outer turning points, i.e. \( r_{\text{max}} \), obtained from the RKR potential curve, corresponding to experimentally observed vibrational levels. Since \( C \) in the FP potential function (eq. (3)) is an adjustable constant, \( C \) and \( D_e \) have been evaluated by using iteration method such that mean square deviation, given by

\[
\Delta Y_j = \frac{\sqrt{(U_j - U_{\text{RKR}})^2}}{D_e},
\]

where \( j \) stands for various potential functions, has minimum value. With the rough estimated values of \( D_e \) from the linear extrapolation method, i.e., \( D_e = \frac{\omega_e^2}{4\omega_e x_e} \) and \( C \) from the relation [9]

\[
C_{\text{rel}} = \left( -\frac{1}{12} + x \right) - \frac{120}{144} \frac{37}{48} x^2 - 2 \frac{17}{12} x + \frac{17}{144} G, \tag{5}
\]

where

\[
x = \frac{1 + F}{a r_e}, \quad F = \frac{\alpha_e \omega_e}{6B_e^2}, \quad \text{and} \quad G = \frac{8\omega_e x_e}{B_e},
\]

for the whole potential curve as the starting points, the potential energies corresponding to FP potential have been obtained by changing \( D_e \) and \( C \) in steps of \( \pm 100 \text{ cm}^{-1} \) and \( \pm 0.1 \), respectively. The resulting values are correlated with the experimental results and the values of \( D_e \) and \( C \) corresponding to minimum value of \( Y_j \) are chosen for the second scan. In the second and subsequent scans, the values of \( D_e \) and \( C \) are varied in steps of decreasing magnitudes. The process is continued till \( Y_j \) is minimum. The last scan has been carried out by changing \( D_e \) by \( \pm 1 \text{ cm}^{-1} \) and \( C \) by \( \pm 0.001 \). The value of \( D_e \) that corresponds to minimum deviation \( Y_j \) in the final scan is regarded as the best estimate of \( D_e \) and relevant \( C \) value.

3. Results and discussion

Dissociation energies of fifteen electronic states of molecules \( \text{Li}_2, \text{Na}_2, \text{K}_2, \text{Rb}_2, \text{CS}_2, \text{Cl}_2, \text{I}_2, \text{IC}_1, \text{HF}, \text{H}_2, \text{CO}, \text{XeO} \) have been obtained employing the molecular constants listed in table 1 and the results are presented in table 2. For comparison, values of \( D_e \) obtained from Lippincott’s analytical potential function [10]

\[
U(r) = D_e(1 - e^{-a})\{1 - abx^{1/2}\exp[-bx^{1/2}]\}, \tag{6}
\]

where

\[
F = \frac{\alpha_e \omega_e}{6B_e^2}, \quad a = \frac{F}{1 + (5F/4)}, \quad N = \frac{2}{r_e} \left( \frac{F}{ab} \right)^2 \quad \text{and} \quad x = \frac{N(r - r_e)^2}{2r}, \quad b = 1.065;
\]

which is considered to be best among the three parameter potential functions for the prediction of \( D_e \) are also included in table 2. Furthermore, anharmonicity constant \( \omega_e x_e \).
Table 2. Comparison of experimental values of $D_e$ with calculated values and the mean deviations \( \Delta X = (D_{\text{exptl}} - D_{\text{cal}})/D_{\text{cal}} \)

where $D_{\text{cal}}(i)$ stands for, $D_{\text{FP}}(\Pi)$, $D_{\text{Lipp}}(\Pi)$, $D_{\text{Lippincot}}(\Pi)$ for fifteen electronic states.

<table>
<thead>
<tr>
<th>State</th>
<th>$C_{\text{min}}$ (cm$^{-1}$)</th>
<th>$C_{\text{max}}$ (cm$^{-1}$)</th>
<th>$\Delta X_{\text{FP}}$ (%)</th>
<th>$\Delta X_{\text{Lipp}}$ (cm$^{-1}$)</th>
<th>$\Delta X_{\text{Lippincot}}$ (%)</th>
<th>$E_{\text{max}}$</th>
<th>$E_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+_g$</td>
<td>-0.350</td>
<td>8613</td>
<td>1.1</td>
<td>18.7</td>
<td>-0.472</td>
<td>0.03</td>
<td>0.9998</td>
</tr>
<tr>
<td>$^3\Sigma^+_g$</td>
<td>0.350</td>
<td>8613</td>
<td>1.1</td>
<td>18.7</td>
<td>0.472</td>
<td>0.9998</td>
<td>0.03</td>
</tr>
<tr>
<td>$^1\Pi$</td>
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<td>10111</td>
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</tr>
<tr>
<td>$^1\Sigma^+_u$</td>
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<td>8613</td>
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<td>18.7</td>
<td>-0.472</td>
<td>0.03</td>
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<td>0.9998</td>
<td>0.03</td>
</tr>
</tbody>
</table>

$D_e$ values are derived from: *NDE long range technique; **RKR potential curve; +Extrapolation from the RKR curve; ++Limiting curve of dissociation.
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Table 3. Comparison of experimental values of $\omega_x \chi_e$ with calculated values and the mean deviations $[\Delta X = (\omega_x \chi_e (\text{exptl}) - \omega_x \chi_e (i)) / (\omega_x \chi_e (\text{exptl}))$; where $\omega_x \chi_e (i)$ stands for $\omega_x \chi_e (\text{FPC}_{\text{rel}})$, FP; $\omega_x \chi_e (\text{FPC}_{\text{min}})$, FP; using equation (7) for the corresponding electronic states given in table 1.

<table>
<thead>
<tr>
<th>$\omega_x \chi_e (\text{exptl})$ cm$^{-1}$</th>
<th>$\omega_x \chi_e (\text{FPC}_{\text{rel}})$ cm$^{-1}$</th>
<th>$\omega_x \chi_e (\text{FPC}_{\text{min}})$ cm$^{-1}$</th>
<th>$\Delta X$ (FP)</th>
<th>$\Delta X$ (FP)</th>
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</thead>
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<tr>
<td>2.6100</td>
<td>3.2150</td>
<td>2.7680</td>
<td>23.1</td>
<td>6.1</td>
</tr>
<tr>
<td>0.7254</td>
<td>0.8816</td>
<td>0.7895</td>
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<td>6.4</td>
</tr>
<tr>
<td>0.3276</td>
<td>0.3859</td>
<td>0.3536</td>
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<td>7.9</td>
</tr>
<tr>
<td>2.6943</td>
<td>3.5437</td>
<td>2.9418</td>
<td>31.5</td>
<td>9.2</td>
</tr>
<tr>
<td>4.8000</td>
<td>4.4261</td>
<td>5.0540</td>
<td>7.8</td>
<td>5.2</td>
</tr>
<tr>
<td>0.6079</td>
<td>0.7973</td>
<td>0.7063</td>
<td>31.2</td>
<td>16.2</td>
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<tr>
<td>1.4920</td>
<td>1.9104</td>
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<td>8.7</td>
</tr>
<tr>
<td>2.1210</td>
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<td>2.1110</td>
<td>18.8</td>
<td>12.2</td>
</tr>
<tr>
<td>89.8800</td>
<td>98.4446</td>
<td>83.3050</td>
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<td>7.3</td>
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<tr>
<td>120.6020</td>
<td>152.4790</td>
<td>120.2257</td>
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</tr>
<tr>
<td>13.2883</td>
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<td>13.2027</td>
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<tr>
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<td>8.3081</td>
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<td>17.1</td>
</tr>
<tr>
<td>0.0826</td>
<td>0.0950</td>
<td>0.0911</td>
<td>15.1</td>
<td>10.3</td>
</tr>
<tr>
<td>0.1391</td>
<td>0.1678</td>
<td>0.1540</td>
<td>20.6</td>
<td>10.8</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>17.4</td>
<td>8.9</td>
</tr>
</tbody>
</table>

have been computed for these electronic states using the relation

$$\omega_x \chi_e = \frac{\hbar}{8\pi^2 c\mu} a^2 (1 + C + C^2) = B_x \Delta (1 + C + C^2)$$

(7)

obtained in our earlier work [9]. Here, we have used C calculated above for the outer limb. These results together with the experimental values of $\omega_x \chi_e$ and the ones found by us in ref. [9], are compiled in table 3.

Earlier works on the studies of electronic states of the molecules subjected to the present analysis (see the references in table 1) show that the properly executed NDE method of LeRoy et al [2–4] and RKR approach yield accurate values of $D_e$. So we have taken these $D_e$ values as experimental (being the best prediction) to compare our findings and have given these in the second column of the table 2. It may be mentioned that $D_e$ for HF included in this table has been obtained earlier from the limiting curve of dissociation.

A comparison of our results constituting third column of table 2 with experimental values listed in column 2 shows that the extent of agreement depends on the method. For the electronic states $\text{Li}_2 (X^1\Sigma_g^+)$, $\text{Na}_2 (X^1\Sigma_g^+)$, $\text{Cl}_2 (X^1\Sigma_g^+)$, $\text{I}_2 (X^1\Sigma_g^+)$, $\text{ICl} (X^1\Sigma_g^+)$ and $\text{Cs}_2 (X^1\Sigma_g^+)$ for which experimental $D_e$ values have been found with NDE technique (that includes the long range forces) the difference is less than 2%. However, in $A$ and $A'$ electronic states of ICl the deviations are respectively 2.5% and 2.6%. The deviation in the case of the electronic state $A$ can be viewed in the light of reported vibrational perturbations near dissociation and the merging approach (merging the constants from individual absorption band and emission band through least square fit) used to obtain $D_e$ [16]. Similar explanation is valid for state $A'$ also since there is a possibility of perturbation in state $A'$ [17], near the dissociation limit, because there exists a shallow $\Omega = 2$ state [18], which converges to the same dissociation limit.
On the other hand, for the electronic states $K_2(X'\Sigma^+_g)$, $HF(X'\Sigma^+_g)$, $H_2(X'\Pi^+_g)$, $CO(X'\Sigma^+_g)$, $XeO(X'\Sigma^+_g)$, and $Rb_2(X'\Pi^+_g)$, whose $D_e$ have been determined using RKR potential curves the percentage variations lie between 4 and 5.7. On referring back to literature, it is found that the highest observed vibrational levels in $K_2$, CO and $Rb_2$ viz. $v = 37$ at 63334.333 cm$^{-1}$ for CO [13,14], $v = 50$ at 3687.749 cm$^{-1}$ for $K_2$ [11], $v = 72$ at 3313.143 cm$^{-1}$ for $Rb_2$ [12], giving $E_{\text{max}}/D_e \sim 0.70, 0.83, \text{and } 0.84$ respectively, where $E_{\text{max}}$ denotes the energy of highest observed level, are fairly below the respective dissociation limits. That means, RKR potential curve has been drawn accurately only up to the observed levels. Moreover, since RKR does not provide any direct means of extrapolation beyond the observed levels [2], indirect methods have been employed to obtain $D_e$ values which are likely to be at the variance from the accurate values. In the case of XeO and $H_2$ the levels are observed only up to $v = 8$ and $v = 14$, respectively, so that $D_e$ are expected to be more erroneous.

Long range forces have dominant influence [2] on the vibrational levels close to dissociation limit (~ top 10% of the potential well). With a view to examine the performance of the FP potential function close to the dissociation limit, $D_e$ (denoted as $D_e$ (FP1/3) in table 2) and $C$ (referred to as $C_{\text{min}}(1/3)$ in table 2) have been derived considering only the highest one-third of the known vibrational levels. But for the CO electronic state, the results (given in column 10 of table 2) for all other states have been improved significantly. The slight adverse result of CO is understandable since the known data constitute only 70% of the potential well starting from equilibrium position. This observation, besides providing better accuracy of $D_e$, also strengthens the earlier findings [6], that FP potential describes experimental potential curves more accurately especially when the potential domain extends to near the dissociation limit.

Values of vibrational constant $\omega_x x_e$, when computed from the outer limb of the RKR curve show a marked improvement over the ones calculated using inner wall as well as the outer wall (i.e. $r_{\text{min}} < r < r_{\text{max}}$) of the potential curve (table 3). The average mean deviation from the experimental values has been reduced to 8.9% from 17% [9]. Furthermore, since $\omega_x x_e$ has been calculated using outer limb of the potential curve, the findings are in conformity with the fact that, because of anharmonicity, the vibrational spacings and other properties of diatomic molecules [2, 7, 8] are explained mainly by the outer limb of the potential curve.

4. Conclusion

FP potential function of Wei Hua can be used to predict dissociation energy of the electronic states of diatomic molecules. The accuracy of prediction is close to the one obtained by NDE long range expansion technique or by RKR potential curve constructed up to near dissociation limit. Besides, FP potential function, through equation (7), predicts $\omega_x x_e$ value better than the known three parameter analytical functions.

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References