Notes

Computation of Spectroscopic Constants of Some Diatomic Hydrides Using Morse-Kratzer Potential Model

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The spectroscopic constants, viz. the rotational constant \( B_r \), the vibrational constant \( \omega \) and the binding energy \( D_l \) of some diatomic hydrides have been computed using the Morse-Kratzer potential. The computed values are in fair agreement with experimental data and rule out any sensitive dependence on arbitrary exponents used in earlier models.

The rotational and vibrational constants and the binding energies of diatomic hydrides have been evaluated by Prasad et al. using the Woodcock potential and also by Pandey and Pandey using the Born-Mayer potential. In the former, a strong dependence of the rotational constant, \( k_e \), on the polariability term \( a \) and of the cohesive energy, \( W \), on the exponent, \( n \) was obtained. It also necessitated use of a correct functional relationship between \( n \) and \( a \). Further, positive values of \( a \) were obtained only for a narrow band, \( 3.8 < n < 7.1 \). A proper choice of the exponent \( n \) was necessary to determine \( k_e \) and \( W \). This problem was circumvented by considering a combination of the Morse and Kratzer potentials, referred to as the Morse-Kratzer potential. It was found that this potential ruled out any sensitive dependence on the exponent, \( n \) in the Woodcock potential and the computed values of \( k_e \), \( \omega X_e \) and \( W \) for the five alkali hydrides were in accordance with the available cyclic process data. In this communication, we extend the scope of the Morse-Kratzer potential to compute the values of \( k_e \), \( \omega X_e \) and \( D_l \) of fourteen diatomic molecules.

The Morse-Kratzer potential is given by Eq. (1),

\[
U(r) = D_e [1 - \exp(-\beta(r - r_e))]^2 + D_k \left( \frac{r - r_e}{r} \right)^2 \tag{1}
\]

where \( D_e \), \( \beta \) and \( r_e \) are the dissociation energy, Morse parameter and equilibrium distance, respectively. The test of this potential depends upon a satisfactory fit of the values of the experimental constants like \( k_e \), \( \omega X_e \) and \( D_l \) of fourteen diatomic molecules.

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We further impose the criteria (a - c) of Varshni and Shukla on the potential function given in Eq. (1),

(a) \( (dU/dr)_r=r_e=0 \),
(b) \( (d^2 U/dr^2)_{r=r_e} = k_e \),
(c) \( U(\infty) = 2D_k \) \( \tag{2} \)

Having fixed the potential energy curve, the calculation for the rotational constants may be carried out. Following Dunham, we have

\[
k_e = \frac{6B_e^2}{\omega} \left( \frac{(\Delta - 1)^{3/2} + 1 - (\Delta - 1)^{1/2}}{\Delta} \right) \tag{3}
\]

and

\[
\omega X_e = \left( \frac{W}{\mu_A r_e^2} \right) G \tag{4}
\]

where \( \mu_A \) is the reduced mass in atomic weight units and

\[
F = -(1 + X r_e) \tag{5}
\]

\[
G = (5X^2/3 - Y) \tag{6}
\]

\[
W = 2.1078 \times 10^{-16} \tag{7}
\]

\[
X = \left( \frac{d^3 U}{dr^3} \right)_{r=r_e} \tag{8}
\]

\[
Y = \left( \frac{d^4 U}{dr^4} \right)_{r=r_e} \tag{9}
\]

The criteria (a) and (b) of Varshni and Shukla are satisfied automatically by Eq. (1). The third criterion(c) can be used to get an expression for \( k_e \) as mentioned in our earlier paper.

Using Eqs. (3)-(9) we get the following expressions

\[
k_e = \frac{6B_e^2}{\omega} \left[ \frac{(\Delta - 1)^{3/2} + 1 - (\Delta - 1)^{1/2}}{\Delta} \right] \tag{10}
\]

and

\[
\omega X_e = \frac{2.1078 \times 10^{-16}}{\mu_A r_e^2 \Delta^2} \left[ 8(\Delta - 1)^3 + 60(\Delta - 1)^{3/2} - 36(\Delta - 1) - (\Delta - 1)^2 + 24 \right] \tag{11}
\]

where \( \Delta \) is the Southerland parameter and is given by

\[
\Delta = \beta^2 r_e^2 + 1 \tag{12}
\]

The experimental values are the same as quoted by Pandey and Pandey while the values of the spectroscopic constants like \( k_e \), \( B_e \), \( r_e \) and reduced mass \( \mu_A \) are taken from Huber and Herzberg. The agreement between the theoretical and experimental values of \( k_e \) and \( \omega X_e \) is fairly reasonable (see Table 1). The per cent deviation for LiH is high (26.9\%) for \( k_e \) and for AIH the per cent deviation in \( \omega X_e \) is about 17.0\%.

The binding energy \( D_l \) per mol of the diatomic molecule is given by

\[
D_l = -NU(r_e) \tag{13}
\]
Table 1—Calculated and Experimental Values of Spectroscopic Constants of Diatomic Hydrides

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$x_0 (\text{cm}^{-1})$</th>
<th>$\omega X_0 (\text{cm}^{-1})$</th>
<th>$D_1 (\text{kJ mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>0.213</td>
<td>0.269</td>
<td>23.2</td>
</tr>
<tr>
<td>BeH</td>
<td>0.303</td>
<td>0.306</td>
<td>36.3</td>
</tr>
<tr>
<td>BH</td>
<td>0.412</td>
<td>0.443</td>
<td>49.4</td>
</tr>
<tr>
<td>CH</td>
<td>0.534</td>
<td>0.592</td>
<td>67.0</td>
</tr>
<tr>
<td>NH</td>
<td>0.643</td>
<td>0.741</td>
<td>78.3</td>
</tr>
<tr>
<td>OH</td>
<td>0.714</td>
<td>0.730</td>
<td>86.4</td>
</tr>
<tr>
<td>HF</td>
<td>0.795</td>
<td>0.792</td>
<td>90.1</td>
</tr>
<tr>
<td>NaH</td>
<td>0.135</td>
<td>0.129</td>
<td>19.7</td>
</tr>
<tr>
<td>MgH</td>
<td>0.167</td>
<td>0.188</td>
<td>32.4</td>
</tr>
<tr>
<td>AlH</td>
<td>0.188</td>
<td>0.201</td>
<td>29.1</td>
</tr>
<tr>
<td>SiH</td>
<td>0.219</td>
<td>0.263</td>
<td>35.5</td>
</tr>
<tr>
<td>PH</td>
<td>0.285</td>
<td>0.304</td>
<td>46.7</td>
</tr>
<tr>
<td>HCl</td>
<td>0.305</td>
<td>0.372</td>
<td>52.8</td>
</tr>
</tbody>
</table>

where $N$ is the Avogadro number. The calculated values are listed in Table 1 along with the experimental values. The maximum percentage deviation in $D_1$ is for PH (9.6%). The agreement appears to be better than the values given earlier.

In conclusion, it may be stated that the Morse-Kratzer potential is more suitable to evaluate the spectroscopic constants of diatomic molecules and is devoid of any sensitive dependence on exponents or arbitrary parameters prescribed in other models.

References