

Comment

Dissociation energy of diatomic molecules – comment on the work of Kaur and Mahajan

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Abstract. When observed spectrum of a diatomic molecule is expressed in terms of the Dunham coefficients Y_{00} , Y_{10} , Y_{20} , Y_{01} , and Y_{11} only, dissociation energy of the molecule is given by $Y_{00} + Y_{10}^2/(-4Y_{20})$. Kaur and Mahajan [1] have used the Dunham coefficients Y_{10} , Y_{20} , Y_{01} , and Y_{11} , for 15 vibrational states of 12 diatomic molecules (Y_{00} is zero for the cases accounted for), but their dissociation energy cannot be reproduced by the expression $Y_{10}^2/(-4Y_{20})$. Probable reason for the discrepancy has been discussed.

Keywords. Dissociation energy; diatomic molecules.

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Kaur and Mahajan [1] determined dissociation energy for 15 vibrational states of 12 diatomic molecules. It is surprising to note down that for calculating dissociation energy D_e of a vibrational state of a molecule, experimental value of the dissociation energy of the vibrational state of the molecule itself has been used as one of the input parameters.

The classical left- and right-hand turning points, r_{\min} and r_{\max} , respectively, of the Rydberg–Klein–Rees (RKR) potential-energy curve, for a diatomic molecule, are given by

$$r_{\min} = (f/g + f^2)^{1/2} - f, \quad r_{\max} = (f/g + f^2)^{1/2} + f,$$

where f and g are termed as Klein integrals, which for the case of a limited number of Dunham coefficients, Y_{00} , Y_{10} , Y_{20} , Y_{01} , and Y_{11} , (when the Y_{20} is negative) are given by [2]

$$f(\text{cm}) = \left(\frac{h}{8\pi^2\mu_e c(-Y_{20})} \right)^{1/2} \ln \left[\frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} - \sqrt{4U(-Y_{20})}}} \right] \quad (1)$$

and

Table 1. Values of the parameters.

Molecular state	$\omega_e = Y_{10}$ (cm^{-1})	$\alpha_e = -Y_{11}$ 10^3 (cm^{-1})	$B_e = Y_{01}$ (cm^{-1})	$\omega_e x_e = -Y_{20}$ (cm^{-1})	D_e (cm^{-1})	$Y_{10}^2/(-4Y_{20})$ (cm^{-1})
$\text{Li}_2 X^1\Sigma_g^+$	351.430	7.040	0.6725	2.6100	8516.780	11829.79
$\text{Na}_2 X^1\Sigma_g^+$	159.177	0.873	0.1547	0.7254	6022.600	8732.19
$\text{K}_2 X^1\Sigma_g^+$	92.405	0.212	0.0562	0.3276	4440.000	6516.09
$\text{Cl}_2 X^1\Sigma_g^+$	559.751	1.516	0.2442	2.6943	20276.440	29072.60
$\text{Cl}_2 B^3\Pi$	255.380	2.511	0.1631	4.8000	3341.170	3396.82
$\text{I}_2 X O_g^+$	214.520	0.113	0.0373	0.6079	12547.335	18925.33
$\text{ICl } X^1\Sigma^+$	384.275	0.532	0.1142	1.4920	17557.600	24743.18
$\text{ICl } A^3\Sigma_1$	211.030	0.744	0.0852	2.1200	3814.700	5251.61
$\text{ICl } A^3\Sigma_2$	224.571	0.674	0.0865	1.8823	4875.520	6698.21
$\text{HF } X^1\Sigma^+$	4138.320	772.400	20.9557	89.8800	49384.000	47634.88
$\text{H}_2 X^1\Sigma_g^+$	4401.265	3051.300	60.8477	120.6020	38297.000	40155.08
$\text{CO } X^1\Sigma^+$	2169.813	17.504	1.93137	13.2883	90529.000	88575.82
$\text{XeO } d^1\Sigma^+$	156.832	5.400	0.1456	9.8678	693.000	623.14
$\text{Cs}_2 X^1\Sigma_g^+$	42.020	0.022	0.0117	0.0826	3649.500	5344.07
$\text{Rb}_2 X^1\Sigma_g^+$	57.7807	0.055	0.0224	0.1391	3950.000	6000.38

$$g(\text{cm}^{-1}) = \left(\frac{8\pi^2 \mu_e c}{h(-Y_{20})} \right)^{1/2} Y_{11} \left(-\sqrt{\frac{U}{(-Y_{20})}} + \left(\frac{Y_{01}}{Y_{11}} - \frac{Y_{10}}{2Y_{20}} \right) \ln \left[\frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} - \sqrt{4U(-Y_{20})}}} \right] \right). \quad (2)$$

The separation between the left and right turning points is given by $2f$. Hence, around the dissociation limit, the value of f tends to become infinite. Thus, from eq. (1), the dissociation energy is given by

$$U = Y_{00} + \frac{Y_{10}^2}{4(-Y_{20})}. \quad (3)$$

For the cases accounted for [1], the value of Y_{00} is zero. Equation (3) for the case $Y_{00} = 0$ is the same as obtained by Rees [3]. The values of the parameters used by Kaur and Mahajan [1] alongwith the value of $Y_{10}^2/(-4Y_{20})$ are given in table 1. Comparison of the experimental value of the dissociation energy D_e with that of $Y_{10}^2/(-4Y_{20})$ shows a large discrepancy.

Now, the question arises: what could be the reason for the discrepancy? We feel that one of the probable reasons may be as follows: In actual practice, observed spectrum of a diatomic molecule is expressed in terms of a large number of Dunham coefficients Y_{i0} and Y_{i1} , where the index i varies from zero to a high value (e.g., up to 8 or 9, or even higher) for better accuracy. For example, the spectrum of the $X^1\Sigma^+$ state of CO was expressed by Farrenq *et al* [4] with Dunham coefficients up to Y_{90} and Y_{71} . Under this situation, it is not possible to get analytical expressions for the Klein integrals f and g , and they are calculated numerically [2, 5–7].

It appears that spectrum of a molecule is expressed in terms of a large number of Dunham coefficients, whereas a limited number of Dunham coefficients have been accounted for by Kaur and Mahajan [1]. Further, for fitting by the given expression, they [1] used known experimental value of the dissociation energy D_e itself, and after finding out the unknown constants, they calculated the dissociation energy.

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