

Relation between spectroscopic constants with limited Dunham coefficients

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Abstract. Statement of Kaur and Mahajan [1] about the definition of Δ used by Chandra [2] is not correct. Even if we take $\Delta = \mu\omega_e^2 r_e^2 / 2D_e$, the relation between Δ and $G(=8\omega_e x_e / B_e)$ is obtained as $\Delta = 4.21452856G$, provided the vibrational energy of a diatomic molecule is expressed in terms of limited Dunham coefficients, Y_{10} , Y_{20} , Y_{01} and Y_{11} . This relation is still different from that of Kaur and Mahajan [3].

Keywords. Diatomic molecules; dissociation energy; equilibrium distance.

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In the Rydberg–Klein–Rees (RKR) potential energy curve for a diatomic molecule, the turning points, r_{\min} and r_{\max} , are given by [4–7]

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

where the Klein integrals f and g are defined as

$$f = \left(\frac{h}{8\pi^2\mu c}\right)^{1/2} \int_0^t [U - E(v, J)]^{-1/2} ds, \quad (1)$$

$$g = \left(\frac{8\pi^2\mu c}{h}\right)^{1/2} \int_0^t [U - E(v, J)]^{-1/2} \frac{\partial E}{\partial [J(J+1)]} ds, \quad (2)$$

where

$$s = v + \frac{1}{2}, \quad t = v' + \frac{1}{2}.$$

h is the Planck's constant, c is the speed of light in vacuum, μ is the reduced mass of the molecule, v is the vibrational quantum number, and v' is the vibrational quantum number of the level (with the rotational quantum number $J = 0$) for which the turning points are to be calculated. The energy of vib-rotational levels in a diatomic molecule is

Suresh Chandra

$$E(v, J) = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2}\right)^i \left[J(J+1)\right]^j.$$

Here, Y_{ij} are known as Dunham coefficients. The energy of the level with vibrational quantum number v' , and the rotational quantum number $J = 0$, is

$$U = \sum_{i=1} Y_{i0} t^i.$$

Spectroscopic parameters, ω_e , α_e , B_e , $\omega_e x_e$ are related to the Dunham coefficients [2] as

$$\omega_e = Y_{10}, \quad \alpha_e = -Y_{11}, \quad B_e = Y_{01}, \quad \omega_e x_e = -Y_{20}.$$

Laboratory spectra of diatomic molecules are generally fitted in terms of a large number of Dunham coefficients, up to Y_{90} for vibrational constants and up to Y_{71} for rotational constants.

The main problem in the evaluation of the integrals f and g is the singularity at the upper limit of the integrals (1) and (2). For dealing with this singularity, several numerical techniques have been developed [8]. For a limited number of Dunham coefficients, Y_{10} , Y_{20} , Y_{01} and Y_{11} , the singularity, however, disappears from the picture and the integrals f and g can be evaluated analytically [8].

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

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

At the equilibrium distance r_e , the energy U tends to achieve its minimum possible value and we have

$$f = \left[\frac{hU}{2\pi^2 \mu c Y_{10}^2} \right]^{1/2}, \quad g = \left[\frac{32\pi^2 \mu c U}{h} \right]^{1/2} \frac{Y_{01}}{Y_{10}}.$$

The dissociation energy D_e and the equilibrium distance r_e are [7]

$$D_e = \frac{Y_{10}^2}{4(-Y_{20})}, \quad r_e = \left[\frac{h}{8\pi^2 \mu c Y_{01}} \right]^{1/2}. \quad (3)$$

For the electronic states of the molecules considered by Kaur and Mahajan [3], we can calculate the dissociation energy and the equilibrium distance with the help of eq. (3). The atomic masses (in atomic mass units) used here for the calculation of reduced mass of molecules are given in table 1.

Comparison of our values of r_e with those of Kaur and Mahajan [3] shows a reasonable agreement within few percentage. However, from the point of view of the

Relation between spectroscopic constants

Table 1. Atomic masses in a.m.u.

Atom	Symbol	Mass
Hydrogen	H	1.0080
Lithium	Li	6.941
Carbon	C	12.0111
Nitrogen	N	14.0067
Oxygen	O	15.9994
Fluorine	F	18.9984
Sodium	Na	22.9898
Chlorine	Cl	35.453
Potassium	K	39.102
Argon	Ar	39.948
Zinc	Zn	65.37
Bromine	Br	79.904
Rubidium	Rb	85.4678
Cadmium	Cd	112.40
Iodine	I	126.9045
Xenon	Xe	131.30
Cesium	Cs	132.905
Mercury	Hg	200.59

required accuracy in general, the difference is quite significant. One of the possible reasons for the difference may be the values of the parameters used. In the present investigation, we have taken: $h = 6.626205 \times 10^{-27}$ erg-s; $c = 2.9979250 \times 10^{10}$ cm/s; $\pi = 3.1415926536$ and 1 a.m.u. = 1.660531×10^{-24} g. Comparison of our values of D_e with those of Kaur and Mahajan [3] shows a large discrepancy in some cases.

For the Sutherland parameter $\Delta (= k_e r_e^2 / 2D_e)$, in the second paragraph of §2 on p. 480 of their paper, Kaur and Mahajan [3] wrote “When G , k_e (i.e. ω_e) and r_e are known” and there was no other mention whatsoever about k_e . This much information obviously leads any one to write

$$\Delta = \frac{\omega_e r_e^2}{2D_e}.$$

Thus, the statement of Mahajan [1] that this wrong definition for Δ was given by Chandra [2] is not correct. The learned referee of the paper of Chandra [2] also mentioned that he/she had no idea about the Sutherland parameter. Further, Herzberg [9] on p. 459 has not given any definition or relation for the Sutherland parameter, and he wrote “Several authors have suggested empirical formulae relating r_e and k_e with the heat of dissociation for the ground states of various types of diatomic molecules [...., Sutherland (1443),].” In the bibliography of the book, Herzberg [9] gave ref. [1443] as: G.B.B.M. Sutherland, *J. Chem. Phys.* **8**, 161 (1940). Even this reference of Sutherland was not available in [3].

Let us now take

$$\Delta = \frac{\mu \omega_e^2 r_e^2}{2D_e} \quad (4)$$

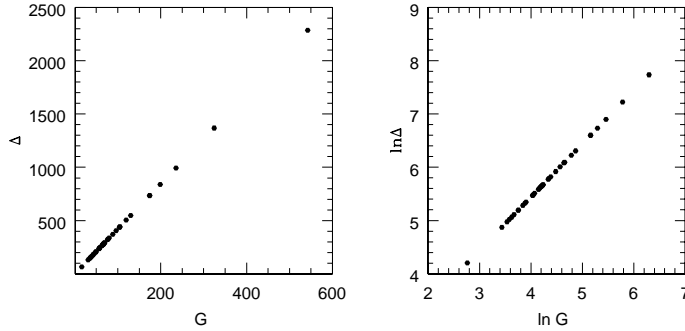


Figure 1. Plots of Δ vs. G and $\ln \Delta$ vs. $\ln G$.

and define a parameter $G(= 8\omega_e x_e/B_e)$. Using eq. (3), we get a relation

$$\Delta = \frac{h}{32\pi^2 c} G. \quad (5)$$

For expressing the reduced mass μ in a.m.u. and r_e in \AA for calculating Δ (eq. (4)), the right-hand side of eq. (5) is divided by 1.660531×10^{-40} . Using the values of the constants, we get

$$\Delta = 4.21452856G. \quad (6)$$

On taking logarithm, we have

$$\ln \Delta = 1.43853772 + \ln G. \quad (7)$$

Obviously, relation (7) is different from the relation

$$\ln G = 1.91578(\pm 0.09727) + 0.97111(\pm 0.03809) \ln \Delta \quad (8)$$

given by Kaur and Mahajan [3]; in particular, our constant 1.43853772 is different from their constant 1.91578. In figure 1, we have plotted Δ vs. G and $\ln \Delta$ vs. $\ln G$ for the electronic states given by Kaur and Mahajan [3].

Let us look into the second relation also of Kaur and Mahajan [3]. Using the relations for Δ (eq. (4)) and r_e (eq. (3)), we have

$$\frac{\Delta}{r_e} = (-Y_{20}) \left(\frac{h\mu}{2\pi^2 c Y_{01}} \right)^{1/2}$$

showing that the ratio varies with the molecule and its electronic state, which is totally against the findings of Kaur and Mahajan [3] who found this ratio as independent of alkali group diatomic molecule and its electronic state.

Spectrum of a diatomic molecule is in general expressed in terms of a large number of Dunham coefficients, up to Y_{90} for vibrational constants and up to Y_{71} for rotational constants. Hence these expressions for the limited Dunham coefficients Y_{10} , Y_{20} , Y_{01} and Y_{11} , should not be mixed with the observed values, except for comparison.

Relation between spectroscopic constants

It can be finally concluded that the relations given by Kaur and Mahajan [3] are still not correct. We have given analytical relation between Δ and G . If someone wants to go for the real observations, one has to include a large number of Dunham coefficients which can be done numerically [8].

References

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Editors' Note: This work now terminates the debate and no further communication in this respect will be entertained.