

## Comment on: “Universal relation between spectroscopic constants”

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**Abstract.** Kaur and Mahajan [1] have claimed to derive a universal relation

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

between the Sutherland parameter  $\Delta (= \omega_e r_e^2 / 2D_e)$  and the dimensionless parameter  $G (= 8\omega_e x_e / B_e)$  for the ground as well as excited electronic states of diatomic molecules. Validity of this relation is checked and we find that the relation is not correct. Next, we checked the validity of the relation  $\Delta = 2.2r_e$  for the alkali group diatomic molecules. This relation is also found not to be correct.

**Keywords.** Sutherland parameter; diatomic molecules.

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Spectroscopic parameters,  $\omega_e, \alpha_e, B_e, \omega_e x_e$  are related to the Dunham coefficients in the following manner [1a]:

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

In terms of the Dunham coefficients, the Sutherland parameter  $\Delta$  and the dimensionless parameter  $G$  can be expressed as

$$\Delta = \frac{\omega_e r_e^2}{2D_e} = \frac{Y_{10} r_e^2}{2D_e}, \quad (1)$$

$$G = \frac{8\omega_e x_e}{B_e} = \frac{8(-Y_{20})}{Y_{01}}. \quad (2)$$

The Dunham coefficients and the dissociation energy are expressed in  $\text{cm}^{-1}$  whereas the internuclear distance  $r_e$  between the atoms of diatomic molecule is given in Å.

Kaur and Mahajan [1] have claimed to derive a universal relation between  $\Delta$  and  $G$  as

$$\ln G = 1.91578(\pm 0.09727) + 0.97111(\pm 0.03809) \ln \Delta \quad (3)$$

with the correlation coefficient as 0.97. Within the error limits, eq. (3) can be written as

$$\ln G = 2 + \ln \Delta. \quad (4)$$

Using eqs (1) and (2) in (4), and on rearranging, we get

$$r_e = \frac{4}{e} \sqrt{\frac{D_e(-Y_{20})}{Y_{10}Y_{01}}}. \quad (5)$$

Hence, when eq. (4) (which is nothing but eq. (3) within the error limits) is correct,  $r_e$  can be calculated with the help of eq. (5) by using the given values of  $Y_{10}, Y_{01}, Y_{20}$  and  $D_e$ .

When the observed spectra of a diatomic molecule is expressed in terms of the Dunham coefficients,  $Y_{10}, Y_{20}, Y_{01}$  and  $Y_{11}$  only, the dissociation energy  $D_e$  of the molecule is given by [3,4]

$$D_e = \frac{Y_{10}^2}{4(-Y_{20})}. \quad (6)$$

This equation is valid for those electronic states of diatomic molecules for which the Dunham coefficient  $Y_{00} = 0$ . For the electronic states of diatomic molecules considered by Kaur and Mahajan [1], the value of  $Y_{00}$  is zero, and they have accounted for the Dunham coefficients,  $Y_{10}, Y_{20}, Y_{01}$  and  $Y_{11}$  only. Using eq. (6) for  $D_e$  in (5), we get

$$r_e = \frac{2}{e} \sqrt{\frac{Y_{10}}{Y_{01}}}. \quad (7)$$

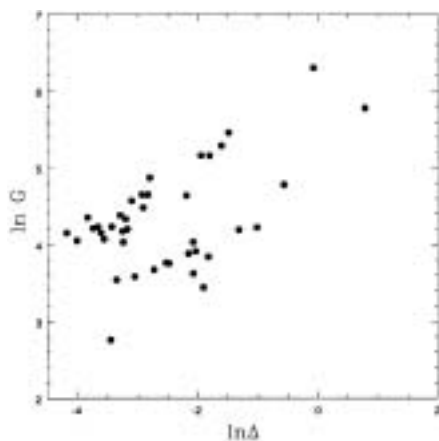
Now, the internuclear distance  $r_e$  can be calculated with the help of eq. (7) as well.

In table 1, we have given the values of  $Y_{10}, Y_{01}, Y_{20}, D_e$  and  $r_e$  (reported by Kaur and Mahajan [1]), and in columns 7 and 8 are the values of  $r_e$  calculated from eqs (5) and (7), respectively, for the electronic states of diatomic molecules considered by Kaur and Mahajan [1]. Comparison of the values of  $r_e$  given in the columns 6 and 7 shows a large discrepancy between them. It shows that the relation between  $\Delta$  and  $G$  given by Kaur and Mahajan [1] is not correct. The values of  $r_e$  in columns 7 and 8 show a good correlation, supporting the expression (6) for the dissociation energy  $D_e$ . The difference between the two sets (columns 7 and 8) can be understood as follows. Spectra of diatomic molecules is generally expressed in terms of a large number of Dunham coefficients instead of the four only [3]. Under that situation, eq. (6) cannot be used for the dissociation energy of diatomic molecules, as it is valid when the spectra is expressed in terms of  $Y_{10}, Y_{20}, Y_{01}$  and  $Y_{11}$  only.

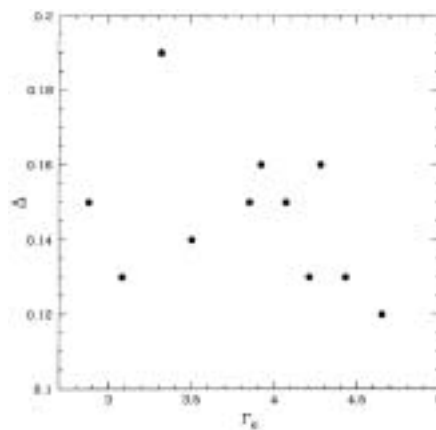
In order to spot out reason for the failure of eq. (3), we plotted a graph (figure 1) for  $\ln G$  vs.  $\ln \Delta$  for the molecular states considered by Kaur and Mahajan [1]. The points in figure 1 obviously cannot be fitted through a linear relation between  $\ln G$  and  $\ln \Delta$  as done by Kaur and Mahajan [1]. It shows that figure 2 of the paper of

**Table 1.** Values of  $Y_{10}$ ,  $Y_{01}$ ,  $Y_{20}$ ,  $D_e$  and  $r_e$ . Values of  $r_e$  in column 6 are from Kaur and Mahajan [1] whereas values in columns 7 and 8 are from eqs (5) and (7), respectively.

Molecular state	$Y_{10}$ ( $\text{cm}^{-1}$ )	$Y_{01}$ ( $\text{cm}^{-1}$ )	$(-Y_{20})$ ( $\text{cm}^{-1}$ )	$D_e$ ( $\text{cm}^{-1}$ )	$r_e$ ( $\text{\AA}$ )	$r_e$ ( $\text{\AA}$ )	$r_e$ ( $\text{\AA}$ )
$\text{Li}_2 \text{X}^1\Sigma_g^+$	351.430	0.6726	2.6100	8516.780	2.673	14.270	16.818
$\text{Na}_2 \text{X}^1\Sigma_g^+$	159.177	0.1547	0.7254	6022.600	3.079	19.600	23.601
$\text{K}_2 \text{X}^1\Sigma_g^+$	92.405	0.0562	0.3276	4440.000	3.924	24.627	29.834
$\text{Rb}_2 \text{X}^1\Sigma_g^+$	57.781	0.0224	0.1391	3950.000	4.210	30.319	37.368
$\text{Cs}_2 \text{X}^1\Sigma_g^+$	42.020	0.0117	0.0826	3649.500	4.648	36.438	44.093
$\text{Cl}_2 \text{X}^1\Sigma_g^+$	559.751	0.2442	2.6943	20276.439	1.987	29.418	35.226
$\text{Cl}_2 \text{B}^3\Pi$	255.380	0.1631	4.8000	3341.170	2.431	28.875	29.114
$\text{I}_2 \text{XO}_g^+$	214.520	0.0374	0.6079	12547.335	2.666	45.390	55.745
$\text{ICl X}^1\Sigma^+$	384.275	0.1142	1.4920	17557.600	2.321	35.952	42.680
$\text{ICl A}^3\Pi_1$	211.030	0.0853	2.1200	3814.700	2.685	31.192	36.598
$\text{ICl A}^3\Pi_2$	224.571	0.0865	1.8823	4875.520	2.665	31.984	37.489
$\text{HF X}^1\Sigma^+$	4138.320	20.9557	89.8800	49384.000	0.917	10.528	10.339
$\text{H}_2 \text{X}^1\Sigma_g^+$	4401.265	60.8477	120.6020	38297.000	0.742	6.111	6.258
$\text{CO X}^1\Sigma^+$	2169.813	1.9314	15.2883	90529.000	1.128	26.742	24.661
$\text{XeO d}^1\Sigma^+$	156.832	0.1456	9.8678	693.000	2.852	25.465	24.148
$\text{Ar}_2 \text{XO}_g^+$	30.680	0.0597	2.4200	99.500	3.761	16.879	16.686
$\text{O}_2 \text{X}^3\Sigma_g^-$	1579.247	1.4456	11.5008	42047.000	1.207	21.416	24.318
$\text{O}_2 \text{b}_1\Sigma_g^+$	1432.775	1.4004	14.0065	28852.000	1.227	20.883	23.534
$\text{O}_2 \text{A}^3\Sigma_u^+$	815.648	0.9105	19.8513	6643.000	1.521	19.609	22.022
$\text{O}_2 \text{B}^3\Sigma_u^-$	709.050	0.8189	10.6100	8121.000	1.604	17.926	21.650
$\text{O}_2^+ \text{X}^2\Pi_g$	1905.335	1.6905	16.3040	54681.000	1.117	24.481	24.701
$\text{NO X}^2\Pi_{1/2}$	1904.204	1.6719	14.0750	53323.758	1.151	22.593	24.830
$\text{NO B}^2\Pi$	1037.200	1.0920	7.7000	26544.889	1.417	19.768	22.675
$\text{N}_2 \text{X}^1\Sigma_g^+$	2358.570	1.9982	14.3240	78742.305	1.098	22.764	25.278
$\text{N}_2 \text{A}^3\Sigma_u^+$	1460.640	1.4546	13.8720	29772.230	1.287	20.516	23.315
$\text{N}_2 \text{a}^1\Pi_g$	1694.208	1.6169	13.9490	48974.914	1.220	23.238	23.816
$\text{N}_2 \text{B}^3\Pi_g$	1733.390	1.6374	14.1220	39534.941	1.213	20.639	23.939
$\text{OH X}^2\Pi_i$	3737.760	18.9108	84.8813	37308.074	0.970	9.849	10.344
$\text{OH A}^2\Sigma^+$	3178.860	17.3580	92.9170	20412.938	1.012	8.627	9.957
$\text{Br}_2 \text{X}^1\Sigma_g^+$	325.321	0.0821	1.0774	15900.307	2.281	37.267	46.315
$\text{C}_2 \text{X}^1\Sigma_g^+$	1854.710	1.8198	13.3400	50104.484	1.242	20.708	23.489
$\text{CO d}^3\Delta_i$	1171.940	1.3108	10.6350	28368.336	1.370	20.622	22.000
$\text{CO A}^1\Pi$	1518.240	1.6115	19.4000	25617.027	1.235	20.972	22.583
$\text{CO e}^3\Sigma^-$	1117.720	1.2836	10.6860	25391.113	1.384	20.236	21.711
$\text{ZnH } \Sigma^+$	1607.600	6.6794	55.1400	7670.453	1.594	9.235	11.414
$\text{CdH a}^3\Sigma^+$	1430.700	5.4370	46.3000	6184.712	1.762	8.928	11.935
$\text{HgH a}^3\Sigma^+$	1387.100	5.5490	83.0100	3726.940	1.740	9.329	11.633
$\text{HCl a}^3\Sigma^+$	2989.700	10.5910	52.0500	37239.141	1.275	11.513	12.362
$\text{HBr a}^3\Sigma^+$	2649.700	8.4730	45.2100	31613.539	1.414	11.741	13.011
$\text{HI a}^3\Sigma^+$	2309.500	6.5510	39.7300	25811.600	1.604	12.115	13.815



**Figure 1.** Variation of  $\ln G$  vs.  $\ln \Delta$  for the molecular states considered by Kaur and Mahajan [1].



**Figure 2.** Variation of  $\Delta$  vs.  $r_e$  for the molecular states of alkali group diatomic molecules considered by Kaur and Mahajan [1].

Kaur and Mahajan [1] which is the basis of their entire investigation is completely wrong. It is also interesting to note that the values of  $\Delta$  are less than 1 in most cases unlike what Kaur and Mahajan [1] have shown in their figure 2.

**(i) About the relation  $\Delta = 2.2r_e$  for alkali group diatomic molecules**

The relation  $\Delta = 2.2r_e$  can be expressed as

$$\Delta = 2.2r_e, \quad (8)$$

$$\frac{Y_{10}r_e^2}{2D_e} = 2.2r_e,$$

$$D_e = \frac{Y_{10}r_e}{4.4}. \quad (9)$$

In table 2, we have given the values of  $r_e$ ,  $Y_{10}$ , and  $D_e$  (reported by Kaur and Mahajan [1]), and in the last column the value of  $D_e$  calculated from eq. (9) for the alkali group diatomic molecules considered by Kaur and Mahajan [1]. Comparison of the results given in columns 4 and 5 shows a large discrepancy between the two sets given in the columns, and therefore, the relation  $\Delta = 2.2r_e$  for alkali group diatomic molecules considered by Kaur and Mahajan [1] is not correct. In order to understand the situation, we plotted a graph (figure 2) for  $\Delta$  vs.  $r_e$  for the molecular states of alkali group diatomic molecules considered by Kaur and Mahajan [1]. Figure 2 shows that there is no linear relation between  $\Delta$  and  $r_e$  unlike what Kaur and Mahajan [1] have given.

Finally, it can be concluded that the relations (3) as well as (8) given by Kaur and Mahajan [1] are not found to be correct for the same sets of molecules considered by them.

**Table 2.** Values of  $r_e$ ,  $Y_{10}$ , and  $D_e$ . Values of  $D_e$  in column 4 are from Kaur and Mahajan [1] whereas values in column 5 are from equation (9).

Molecular state	$r_e$ (Å)	$Y_{10}$ (cm <sup>-1</sup> )	$D_e$ (cm <sup>-1</sup> )	$D_e$ (cm <sup>-1</sup> )
Li <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.6729	351.430	8516.780	213.486
LiNa X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	2.8850	256.990	7067.810	168.504
LiK X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.3169	211.910	6150.000	159.746
Na <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.0788	159.177	6022.600	111.380
NaK X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.4968	124.012	5274.900	98.556
NaCs X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.8500	98.885	4950.000	86.524
K <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	3.9244	92.405	4440.000	82.417
KRb X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.0700	75.500	4071.000	69.838
KCs X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.2800	66.200	3824.000	64.395
Rb <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.2099	57.780	3950.000	55.284
RbCs X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.4271	50.012	3833.000	50.320
Cs <sub>2</sub> X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	4.6480	42.020	3649.500	44.388

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## References

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