Calculation of rotational constants by asymptotic expansion[a)]

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(Received 23 October 1978)

An equation has been derived for the calculation of rotational constants, B_v, using an asymptotic expansion for Morse oscillators. B_v values calculated by the new equation have been compared with those calculated numerically by other methods, and those obtained experimentally.

An asymptotic expansion method was introduced by Chang and Karplus[1] for the calculation of Franck–Condon factors (FCFs). They applied the method for the calculation of FCFs for the N_2, $B^3\Pi_g$–$A^3\Sigma_u^+$ band system and the results were in excellent agreement with those of Jarmain and Nicholls[2] and Biberman and Yakubov.[3] Later their[1] method was used by Chakraborty and Pan[4] for the calculation of FCFs for the transitions N_2, $C^3\Pi_u$–$B^3\Pi_g$ and CN, $B^2\Sigma^+$–$X^2\Sigma^+$ and the calculated values were also in good agreement with Fraser and Jarmain[5] and Jarmain and Nicholls.[2] In a later publication Chakraborty, Pan, and Chang[6] extended the asymptotic expansion method to calculate band strength factors[7] (BSFs) when the electronic dipole moment function, $\mathrm{Re}(r)$, can be expressed as $\mathrm{Re}(r)=A\exp(-Br)$ where A, B are constants and r is real internuclear distance. They also used the Morse–Perkeris oscillator[8] with a slight modification of Shumaker[7] and applied their equations to the calculation of FCFs and BSFs for N_2, $B^3\Pi_g$–$A^3\Sigma_u^+$ and OH, $A^2\Sigma^+$–$X^2\Pi_i$ band systems. Results obtained agreed well with those of Learner[9] though the coefficients A and B were taken from expressions $\mathrm{Re}(\bar{r})=A\exp(-B\bar{r})$, where $\bar{r}$ represents the r-centroid. (The r-centroid is defined as $\langle\psi_{v'}|r|\psi_{v''}\rangle/\langle\psi_{v'}|\psi_{v''}\rangle$, which in a way is the expectation value of r during an electronic transition.)

Recently Gallas, Grieneisen, and Chakraborty[10] extended the asymptotic expansion method further to calculate BSFs when the electronic dipole moment function is expressed as $\mathrm{Re}(r)=\sum a_n r^n$. This is quite useful, since most electronic dipole moment functions for diatomic molecules are expressed as a power series in $\bar{r}$ (i.e., r-centroids). A list of these $\mathrm{Re}(\bar{r})$ functions for some diatomic molecules are recorded by Kuznetosova, Kuzmenko, Kuzyakov, and Plastinin.[11] Most of the time $\mathrm{Re}(\bar{r})$ was expressed as $\mathrm{Re}(\bar{r})=a_0+a_1\bar{r}$; later it was found to fit well with $\mathrm{Re}(\bar{r})=a_0+a_1\bar{r}+a_2\bar{r}^2$; and finally Egorov, Tunitskii, and Cherkasov[12] and Danylewych and Nicholls[13] have shown $\mathrm{Re}(\bar{r})$ to fit best for some band systems as $\mathrm{Re}(\bar{r})=a_0+a_1\bar{r}+a_2\bar{r}^2+a_3\bar{r}^3$. Besides exponential and power series forms, several other interesting forms for $\mathrm{Re}(\bar{r})$ exist. For example, see Brown and Landshoff.[14]

In a recent publication Yeager and McKoy[15] derived expressions for the transition moment involving transitions between electronic states as a function of r (real internuclear distance) and not $\bar{r}$ (r centroids). Their data given in Tables I and II (Ref. 15) can be fit using a power series form of r. Equations derived in Ref. 10 can be used to calculate band strength factors, which hopefully will give better results. Equations derived by Gallas, Grieneisen, and Chakraborty[10] are very general and can be conveniently used to calculate FCFs, BSFs and $\bar{r}$-centroids (if needed) and their J (rotational quantum number) dependence.

The purpose of this article is to show how an asymptotic expansion method can be used to derive an expression for the rotational constants B_v which are characteristic of a particular electronic state, where v represents the vibrational quantum number. In practice, values of B_v are calculated using observed term values and are then called B_v (observed) or B_v (measured). Equations used to calculate B_v (observed) are given in Herzberg[16] for different types of transitions. Some practical difficulties in obtaining B_v (observed) have been given by Lagerqvist, Lind, and Barrow.[17] These B_v (observed) are fit using the following equation:

$$B_v=B_e-\alpha_e(v+\tfrac{1}{2})+\gamma_e(v+\tfrac{1}{2})^2+\cdots\ . \tag{1}$$

B_e, α_e, γ_e are obtained from Eq. (1), generally by a least square fit (see other methods in Refs. 16 and 17). Needless to say the equilibrium internuclear distance r_e is obtained from B_e, which is obtained from several B_v values. α_e and γ_e obtained by fitting Eq. (1) are α_e (fitted) and γ_e (fitted).

According to Herzberg[16] a mean B value for the rotational constant, in the vibrational state considered, is

$$B_v=\frac{h}{8\Pi^2c\mu}\int\psi_v^2r^{-2}\,dr\ , \tag{2}$$

where h is Planck's constant, c is the velocity of light, μ is the reduced mass, and ψ_v is the vibrational wave function. Therefore B_v values can be calculated completely theoretically if ψ_v and μ for the diatomic molecule are known. B_v values were calculated by Jarmain[18] using Eq. (2) to test the wave function ψ_v for a Klein–Dunham potential,[19] set up analytically by Rees,[19] and modified by Jarmain.[18] Cashion[20] and Tawde and Tulasigeri[21] also calculated B_v using Eq. (2). The aforemen-

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[a)] Work supported in part by CNPq and FINEP.

[b)] Predoctoral Fellow.

tioned authors[18,20,21] used numerical integration. Jarmain[18] compared the B_v values obtained for a Klein–Dunham potential with those for a Morse potential[22] whereas Tawde and Tulasigeri[21] compared the B_v values obtained for an RKR potential[23,19(a),19(c)] with those obtained for a Morse potential.

Jarmain[18(b)] noted calculation of B_v using Eq. (2) is an important test (suggested by Dr. P. A. Fraser) for a wave function, ψ_v. However, orthogonality tests, sum rule tests (while calculating FCFs), and calculations of term values $G(v)$ are also used. B_v values have also been calculated with the help of Eq. (1) by Wentink and Spindler[24] and Balfour[25] using Dunham coefficients for B_e, α_e and γ_e. Cashion[20] gave a very clear picture of the testing of a diatomic potential energy function and he justly called B_v calculated by Eq. (2) "unambiguous."

Following other authors[1,22] and Rundgren,[26] we can give the radial wave function ψ_v for a Morse oscillator of reduced mass μ:

$$\psi_v(z)=N_v\exp(-z/2)z^{b/2}L^b_{v+b}(z)\ , \qquad (3)$$

where

$$N_v^2=\frac{ab}{\Gamma(v-1)\Gamma(k-v)}\ ,$$

$$a=0.243\,559(\mu\omega_e x_e)^{1/2}\ ,$$

$$b=k-2v-1\ ,$$

$$k=\omega_e/\omega_e x_e\ ,$$

$$z=k\exp[-a(r-r_e)]\ ,$$

$$L^b_{v+b}(z)=(-1)^v\Gamma(k-v)\sum_{n=0}^{v}(-1)^n\binom{v}{n}\frac{z^{v-n}}{\Gamma(k-v-n)}\ .$$

In the above expressions, ω_e, $\omega_e x_e$ are usual spectroscopic constants expressed in cm^{-1}, r_e is the equilibrium internuclear distance in Å units, symbol Γ signifies the gamma function, and $\binom{v}{n}$ represents a binomial coefficient. Following the approach of Chang and Karplus[1] and Wu,[27] when Eq. (3) is substituted in Eq. (2) we have, replacing dr by $-dz/az$,

$$B_v=\left(\frac{16.8575}{\mu}\right)\left(\frac{N_v^2}{a}\right)\Gamma^2(k-v)\sum_{\lambda=0}^{v}\sum_{\sigma=0}^{v}(-1)^{\lambda+\sigma}\binom{v}{\lambda}\binom{v}{\sigma}\Big/$$
$$\Gamma(k-v-\lambda)\,\Gamma(k-v-\sigma)$$
$$\times\int\exp\left(-\frac{z}{2}\right)z^p\left[r_e+a^{-1}\ln\left(\frac{k}{z}\right)\right]^{-2}dz\ , \qquad (4)$$

where $p=k-\lambda-\sigma-2$ and $h/8\Pi^2c$ has been replaced by 16.8575 so that μ can be expressed in Aston's scale, r_e can be expressed in Å units, and ω_e, $\omega_e x_e$ can be expressed in cm^{-1}. Since p is a large number, using an asymptotic expansion, the integral in Eq. (4) can be reduced to

$$\int\exp\left(-\frac{z}{2}\right)z^p\left[r_e+a^{-1}\ln\left(\frac{k}{z}\right)\right]^{-2}dz$$
$$=p^{p+1}\exp(-p)\left(\frac{2\Pi}{p}\right)^{1/2}\left[\frac{1}{\rho_0^2}+\left(\frac{a\rho_0/12+(1+3/a\rho_0)}{a\rho_0^3}\right)p^{-1}\right], \qquad (5)$$

where $\rho_0=r_e+a^{-1}\ln(k/p)$. Therefore, the expression for B_v becomes

$$B_v=\frac{16.8575}{\mu}(N_v^2/a)\Gamma^2(k-v)\sum_{\lambda=0}^{v}\sum_{\sigma=0}^{v}\binom{v}{\lambda}\binom{v}{\sigma}(-1)^{\lambda+\sigma}\Big/$$
$$\Gamma(k-v-\lambda)\Gamma(k-v-\sigma)p^{p+1}\exp(-p)\left(\frac{2\Pi}{p}\right)^{1/2}$$
$$\times\left[\frac{1}{\rho_0^2}+\left(\frac{a\rho_0/12+(1+3/a\rho_0)}{a\rho_0^3}\right)p^{-1}\right]\ . \qquad (6)$$

Using Eq. (6) a computer program was written in Algol for the Burroughs B6700 Computer. The inputs in the program are μ, ω_e, $\omega_e x_e$, and r_e. We calculated B_v (for v up to 8) using Eq. (6) for some states of AlO, BaO and O_2 molecule. The spectroscopic constants used in this study are given in Table I. In Table II we have compared our values with those of Tawde and Tulasigeri[21] for the AlO, $^2\Sigma^+$ and $X\,^2\Sigma^+$ states. For the upper, $^2\Sigma^+$, state the values given by them for the Morse potential obtained by numerical integration agree very well with ours calculated by Eq. (6). There is also good agreement with the observed B_v. For, the $X\,^2\Sigma^+$ state, our values agree very well with the B_v (observed) and with that obtained by numerical integration for the RKR potential. It seems their values for B_4 and B_5 for the Morse potential obtained by numerical integration for the AlO, $X\,^2\Sigma^+$ state are wrong.

TABLE I. Spectroscopic constants for AlO, BaO, and O_2 used in this study.

Molecule	Electronic state	$\omega_e(\mathrm{cm}^{-1})$	$\omega_e x_e$ (cm^{-1})	r_e(Å)	μ
AlO	$^2\Sigma^+$	819.60	5.80	1.7224	10.0452
	$X\,^2\Sigma^+$	979.23	6.97	1.6176	
BaO	$A\,^1\Sigma$	500.00	1.60	2.133	14.3311
	$X\,^1\Sigma$	669.81	2.054	1.940	
O_2	$B\,^3\Sigma_u^-$	700.36	8.0023	1.604	8.000000

TABLE II. B_v values (in cm^{-1}) for AlO.

State	v	B_v(observed)[a]	B_v(derived)[a] RKR	Morse	B_v(calculated) (this study)
$^2\Sigma^+$	0	0.5633	0.5625	0.5630	0.5631
	1	0.5582	0.5583	0.5578	0.5579
	2	0.5533	0.5533	0.5526	0.5527
	3		0.5513	0.5474	0.5475
	4				0.5422
	5				0.5370
	6				0.5317
	7				0.5264
	8				0.5210
$X\,^2\Sigma^+$	0	0.6384	0.6384	0.6385	0.6384
	1	0.6328	0.6327	0.6327	0.6326
	2	0.6268	0.6267	0.6269	0.6268
	3	0.6210	0.6205	0.6218	0.6209
	4	0.6153	0.6158	0.6311	0.6150
	5	0.6095	0.6107	0.6385	0.6091
	6		0.6021	0.6033	0.6032
	7				0.5972
	8				0.5913

[a] B_v(observed) and B_v(derived) were reproduced from Ref. (21).

TABLE III. B_v values (cm^{-1}) for BaO.

State	v	B_v(measured)[a]		B_v(calculated)[b]		B_v (calculated) (this study)
$A\,^1\Sigma$	0	0.2578		0.2578		0.2579
	1	0.2564		0.2567		0.2567
	2	0.2556		0.2556		0.2556
	3	0.2541		0.2545		0.2544
	4	0.2532		0.2534		0.2532
	5	0.2523		0.2523		0.2519
	6		0	0.2512		0.2507
	7			0.2501		0.2490
	8			0.2490		
	v	$B_v(c)$	$B_v(b)$	$B_v(d)$	$B_v(e)$	
$X\,^1\Sigma$	0	0.31184	0.311917	0.31184	0.31183	0.31186
	1	0.31048	0.310515	0.31050	0.31045	0.31049
	2	0.30912	0.309106	0.30912	0.30899	0.30912
	3	0.30767	0.307688	0.30770	0.30745	0.30774
	4	0.30624	0.306263	0.30624	0.30583	0.30636
	5		0.304829	0.30474	0.30413	0.30499
	6		0.303388	0.30320	0.30235	0.30361
	7		0.301938	0.30162	0.30049	0.30232
	8		0.300481	0.30000	0.29855	

[a] Measured, Reproduced from Ref. 17.

[b] Calculated by Wentink and Spindler, Ref. 24.

[c] Deduced from optical spectra, reproduced from Ref. 17.

[d] Calculated by Eq. (1) of the text, when B_e, α_e, and γ_e are, respectively, 0.32419, 1.30×10^{-3}, and -0.2×10^{-4} taken from Ref. 17.

[e] Calculated by Eq. (1) of the text, B_e and α_e are that of Ref. 17 and refined $\gamma_e = -4.0\times10^{-5}$ given in Ref. 28.

In Table III we have compared B_v, obtained by our Eq. (6) for BaO, $A\,^1\Sigma$ and $X\,^1\Sigma$ states, with that calculated by Wentink and Spindler[24] using Dunham Coefficients for B_e, α_e, and γ_e. Agreement between their values and B_v (observed) is excellent. They have reviewed the spectroscopy and potential well constants for the $A\,^1\Sigma$–$X\,^1\Sigma$, band system of BaO and recalculated the ω_e, $\omega_e x_e$, $\omega_e y_e$ for both the A and X state. However we did not use their constants ($\omega_e x_e$ and ω_e). We used the constants given in Table XI of Ref. 17 (please see Table I). It is interesting to note that if the values reported in Table III are rounded up to four decimal places for the $X\,^1\Sigma$ state, our results agree quite well with theirs and with B_v (observed). Other important points to note that B_v calculated using $B_v = B_e - \alpha_e(v+\frac{1}{2}) + \gamma_e(v+\frac{1}{2})^2$ with refined γ_e of Sakurai, Johnson, and Broida[28] differs from all others for v greater than 4.

TABLE IV. B_v values (cm^{-1}) for O_2 for the upper state of Schumann–Runge band.

State	v	B_v(observed)[a]	B_v(derived)[a] Klein–Dunham	Morse	B_v(calculated) (this study)
$B\,^3\Sigma_u^-$	0	0.813	0.813	0.813	0.8129
	1	0.798	0.799	0.801	0.8006
	2	0.785	0.784	0.788	0.7882
	3	0.770	0.770	0.776	0.7758
	4	0.754	0.754	0.763	0.7632
	5	0.735	0.737	0.751	0.7506
	6	0.719	0.718	0.738	0.7378
	7	0.702	0.699	0.725	0.7250
	8	0.671	0.676	0.712	0.7121

[a] Reproduced from Ref. 18(b).

Finally in Table IV we have presented B_v calculated by us for the $B\,^3\Sigma_u^-$ state of O_2 with B_v (observed) and B_v (calculated) by Jarmin[18(b)] for the both Klein–Dunham and Morse potential by numerical integration. B_v calculated by Eq. (6) agree extremely well with Jarmain's calculations for the Morse potential but is really inadequate for $v > 3$ when compared with observed and calculated from Klein–Dunham potential. We agree that Klein–Dunham wave function is a satisfactory representation for the aforementioned state of O_2.

Finally in the Appendix we would like to show that Eq. (6) for the calculation of B_v reduces to a very simple form for $v = 0$, when Stirling's approximation is assumed.

ACKNOWLEDGMENTS

We are indebted to Dr. G. Bandyopadhyay for sending needed references. We wish to thank José Schifino and F. R. Volcato for helpful discussions.

APPENDIX

For $v = 0$, Eq. (6) for B_v is reduced to

$$B_0 = \frac{16.8575}{\mu}\;\frac{N_0^2}{a}\;\Gamma^2(k)\left[\binom{0}{0}\Big/\Gamma(k)\right]^2 \times (k-2)^{k-1}\exp[-(k-2)]\left(\frac{2\Pi}{k-2}\right)^{1/2} \times\left[\frac{1}{\rho_0^2} + \left(\frac{a\rho_0/12 + (1+3/a\rho_0)}{a\rho_0^3}\right)\right](k-2)^{-1}\,, \qquad \text{(A1)}$$

where $\rho_0 = r_e + a^{-1}\ln[k/(k-2)]$ and N_0^2/a in Eq. (A1) becomes $1/(k-2)!$. Therefore Eq. (A1) is simplified to

$$B_0 = \frac{16.8575}{\mu}\,\frac{1}{(k-2)!}\,(k-2)^{k-1}\exp[-(k-2)]\left(\frac{2\Pi}{k-2}\right)^{1/2} \times\left[\frac{1}{\rho_0^2} + \left(\frac{a\rho_0/12 + (1+3/a\rho_0)}{a\rho_0^3}\right)\right](k-2)^{-1}\,. \tag{A2}$$

Using Stirling's approximation, $(k-2)!$ of Eq. (A2) can be written as

$$(k-2)! = [2\Pi(k-2)]^{1/2}(k-2)^{(k-2)}\exp[-(k-2)]\,, \tag{A3}$$

since $k-2$ is a large number. Then Eq. (A2) reduces to

$$B_0 = \frac{16.8575}{\mu}\left[\frac{1}{\rho_0^2} + \left(\frac{a\rho_0/12 + (1+3/a\rho_0)}{a\rho_0^3}\right)\right](k-2)^{-1}\,. \tag{A4}$$

Now Eq. (A4) can be used readily to calculate B_0. For example, for BaO, $X\,^1\Sigma$ state, using Stirling's approximation, $B_0 = 0.31194$ cm^{-1}, whereas $B_0 = 0.31186$ cm^{-1} using Eq. (6). Similarly, for B_1, there are four terms to calculate using Eq. (6) and B_1 becomes 0.310568 cm^{-1}, whereas $B_1 \simeq 0.310488$ cm^{-1} without Stirling's approximation.

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