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On the Franck–Condon Factor and Band Strength Calculations with Vibration–Rotation Interaction for Morse Oscillators*

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The effects of vibration–rotation interaction on the Franck–Condon factors and band strengths for various rotational quantum number J values of the transitions $B\,^3\pi_g - A\,^3\Sigma_u{}^+$ for N_2 and $A\,^2\Sigma^+ - X\,^2\pi_i$ for OH have been studied by the asymptotic expansion method.

It has been assumed that the vibration–rotation interaction effects in the Franck–Condon factors and band strengths of molecular band systems are usually negligible for relatively low rotational quantum numbers.[1] However, several authors have investigated the errors resulting from neglect of these effects and have shown them to be appreciable for some molecules.[2-8] Molecular band intensity measurements are frequently used for thermometric purposes in flames[9] and shock tube sources,[10] and in these sources one may expect to find appreciable numbers of diatomic molecules with relatively high rotational quantum numbers. For a general potential-energy function, numerical procedures[5,6] must be used to study the above effects. However, for many molecules it is convenient and sufficient to represent the potential-energy curve of a given electronic state of a diatomic molecule by a Morse function. Even here, cumbersome numerical procedures have been used.[3,7]

In a previous paper[11,12] we have shown that the Franck–Condon factors for Morse oscillators can be obtained by an asymptotic expansion of the necessary integrals. Since the method is very simple to use and gives accurate results for a wide range of vibrational quantum numbers, we extend the method to studies of the vibration–rotation interaction effects in the Franck–Condon factors and molecular band strengths.

For this purpose we use the Morse–Pekeris model[13] with slight modification.[7] In this model a radial wavefunction is given by

$$\psi_{vJ}(r) = N_{vJ} \exp(-\tfrac{1}{2}z) z^{b/2} L_{v+b}^{b}(z), \qquad (1)$$

where

$$z = K_1 \exp[-a(r-r_0)],$$

$$r_0 = r_e(1+\alpha),$$

$$b = K_2 - 2v - 1,$$

$$K_1 = 2[(D_2+C_2)/\omega_e\chi_e]^{1/2},$$

$$K_2 = [2(2D_1-C_1)\omega_e\chi_e K_1],$$

$$D_1 = D \exp(-ar_e\alpha),$$

$$D_2 = D \exp(-2ar_e\alpha),$$

$$C_1 = [A/ar_0(1+\alpha)^2][4-(6/ar_0)],$$

$$C_2 = [A/ar_0(1+\alpha)^2][(3/ar_0)-1],$$

$$\alpha = 4AB_e/\omega_e^2,$$

$$A = B_e J(J+1).$$

Here v and J are vibrational and rotational quantum numbers; D, a, and r_e the usual Morse parameters; ω_e, $\omega_e\chi_e$, and B_e the usual spectroscopic constants in cm^{-1} [1]; N_{vJ} the normalization constant; and $L_{v+b}^{b}(z)$ the generalized Laguerre polynomial.

If we use the primed and double-primed quantities to refer to upper and lower electronic states, the Franck–Condon factors are written as

$$q_{v'v''}{}^{J'J''} = \mid I_{v'v''}{}^{J'J''} \mid^2 = \left| \int_0^\infty \psi_{v'J'}(r)\psi_{v''J''}(r)\,dr \right|^2. \qquad (2)$$

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TABLE I. Franck–Condon factors and band strengths[a] for N_2 and OH.

System	Band v′	v″	J	$q_{v'v''}{}^{JJ}$	$p_{v'v''}{}^{JJ}$
N_2[b]	0	0	0	0.339	0.098
$B\ {}^3\pi_g\!-\!A\ {}^3\Sigma_u{}^+$			100	0.312	0.066
	2	2	0	0.113	0.030
			100	0.131	0.025
	4	5	0	0.048	0.009
			100	0.071	0.009
OH[c]	0	0	$1\frac{1}{2}$	0.907	1.00
$A\ {}^2\Sigma^+\!-\!X\ {}^2\pi_i$			$25\frac{1}{2}$	0.843	0.616
			$50\frac{1}{2}$	0.291	0.042
	2	2	$1\frac{1}{2}$	0.507	0.459
			$25\frac{1}{2}$	0.281	0.171
			$50\frac{1}{2}$	0.126	0.007
	4	5	$1\frac{1}{2}$	0.404	0.039
			$25\frac{1}{2}$	0.355	0.030
			$50\frac{1}{2}$	0.002	0.003

[a] See Ref. 14.

[b] Spectroscopic data are given in Ref. 1. The values $k_1 = 23.7$ a.u. and $k_2 = 3.02$ a.u. in Eq. (6) are used.

[c] Spectroscopic data are given in Ref. 1. The values $k_1 = 1$ a.u. and $k_2 = 2.67$ a.u. in Eq. (6) are used and $P_0{}^{1\frac{1}{2}}{}_0{}^{1\frac{1}{2}}$ is normalized to be 1. [J. Anketell and R. C. M. Learner, Proc. Roy. Soc. (London) A301, 355 (1967).]

Following a previous work[11] we put the integral $I_{v'v''}{}^{J'J''}$ in the form,

$$\left| I_{v'v''}{}^{J'J''} \right| = \frac{N_{v'J'}N_{v''J''}}{a'}\ \xi^{\frac{1}{2}}(K_2''-1)$$

$$\times \sum_{\lambda=0}^{v'}\sum_{\sigma=0}^{v''}(-1)^{\lambda+\sigma}B(v',\lambda)B(v'',\sigma)I(\lambda,\sigma),\quad (3)$$

where

$$\xi = (K_1''/K_1'{}^\gamma)\,\exp(a''r_0''-a'\gamma r_0'),\qquad \gamma = a''/a',$$

$$B(v',\lambda) = (b'+v')_\lambda/\lambda!(v'-\lambda)!,$$

$$B(v'',\sigma) = (b''+v'')_\sigma/\sigma!(v''-\sigma)!\xi^{\sigma'}$$

$$(b+v)_l = (b+v)(b+v-1)\cdots(b+v-l+1),$$

$$(b+v)_0 = 1$$

and

$$I(\lambda,\sigma) = \int_0^\infty \exp[-\tfrac{1}{2}(z+\xi z^\gamma)]z^p dz,$$

$$P = \tfrac{1}{2}(K_2'+\gamma K_2'') - \tfrac{1}{2}(1+\gamma) - 1 - \lambda - \gamma\sigma.\quad (4)$$

Since p is a large positive parameter ($\simeq 100$), we can evaluate the integral $I(\lambda,\sigma)$ by Laplace's method of asymptotic expansion.[11]

The band strengths are given by[14]

$$p_{v'v''}{}^{J'J''} = \left| \int_0^\infty \psi_{v'J'}(r)R_e(r)\psi_{v''J''}(r)dr \right|^2,\quad (5)$$

where $R_e(r)$ is the electric dipole transition moment function. If we represent $R_e(r)$ as[15]

$$R_e(r) = k_1 \exp(-k_2 r),\quad (6)$$

then the above method for $q_{v'v''}{}^{J'J''}$ can be used to calculate $P_{v'v''}{}^{J'J''}$ by replacing p by $q = p + k_2/a'$.

We have applied the method to $B\ {}^3\pi_g\!-\!A\ {}^3\Sigma_u{}^+$ of N_2 and $A\ {}^2\Sigma^+\!-\!X\ {}^2\pi_i$ of OH. The double-precision computations have been carried out on a CDC 6600 computer. Results[16] for some representative transitions are given in Table I. The vibration–rotation interaction effects in the case of N_2 appear to be insignificant at least for lower vibrational quantum numbers, confirming a previous work.[7] For the case of OH, the vibration–rotation interaction effects appear to be truly significant. The values for the (0, 0) band agree well with Learner.[3]

ACKNOWLEDGMENTS

[1] G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. I, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), 2nd ed.

[2] R. C. M. Learner and A. G. Gaydon, Nature 183, 242 (1959).

[3] R. C. M. Learner, Proc. Roy. Soc. (London) A269, 311 (1962).

[4] D. C. Jain and R. C. Sahni, Proc. Phys. Soc. (London) 88, 495 (1966).

[5] D. Villarejo, J. Chem. Phys. 49, 2523 (1968).

[6] D. Villarejo, R. Stockbauer, and M. G. Inghram, J. Chem. Phys. 50, 1754 (1969).

[7] J. B. Shumaker, Jr., J. Quant. Spectry. Radiative Transfer 9, 153 (1969).

[8] J. I. Generosa and R. A. Harris, J. Chem. Phys. 53, 3147 (1970).

[9] A. G. Gaydon, *The Spectroscopy of Flames* (Chapman and Hall, London, 1957).

[10] P. B. Coats and A. G. Gaydon, Proc. Roy. Soc. (London) A293, 452 (1966).

[11] T. Y. Chang and M. Karplus, J. Chem. Phys. 52, 783 (1970).

[12] B. Chakraborty and Y. K. Pan, Theoret. Chim. Acta 18, 162 (1970).

[13] C. L. Pekeris, Phys. Rev. 45, 98 (1934).

[14] It should be noted that for calculations of line intensities it must be multiplied by the usual Hönl–London factor. Here we use the term "band strength," following Schumaker.[7]

[15] Learner[3] recommends this form for the ${}^2\Sigma^+\!-{}^2\pi_i$ transition of the OH radical. In general, $R_e(r)$ may be represented by a linear combination of exponential functions. The present method can be readily generalized for the general representation of $R_e(r)$.

[16] The values of $q_{v'v''}{}^{J'J''}$ and $P_{v'v''}{}^{J'J''}$ for a wide range of quantum numbers are available by request to Y. K. Pan.