

ANALYTICAL FORMULA FOR FRANCK-CONDON FACTORS INVOLVING THE MORSE POTENTIAL

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Abstract—Vibrational overlap integrals for the Morse potential are presented by analytic functions which are written as binomial series containing polygamma function and its derivative functions. Our calculating Franck-Condon factors are compared with RKR analysis, numerical calculation by the Morse potential and experimental results by EELS and PES for the following electronic transitions: $N_2(a^1\Pi_g \leftarrow X^1\Sigma_g^+)$, $C^3\Pi_u \leftarrow X^1\Sigma_g^+$, $b^1\Pi_u \leftarrow X^1\Sigma_g^+$, $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ and $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+ \leftarrow X^1\Sigma^+$ in the ionization processes from N_2 and CO to N_2^+ and CO^+ . Very satisfactory agreement among our results, RKR analysis, Morse analysis and experiments is found.

INTRODUCTION

At the present time, it seems to be common that the calculating Franck-Condon factors have been provided by the numerical calculation based on Rydberg–Klein–Rees (RKR) potential (RKR analysis)^{1–3} while another numerical calculation based on the Morse potential (Morse analysis) by Nicholls⁴ is sometimes useful. On the other hand, some analytic formula have been attempted by the Fraser–Jarman method for the Morse potential based on the “average α ” approximation,^{5,6} the asymptotic expansion for the Morse potential,⁷ the simple harmonic oscillator model^{8–10} and the Kratzer oscillator model.¹¹ For many diatomic molecules, however, it is convenient and sufficient (for m, n not too large) to represent the potential of given electronic state by the Morse potential since the harmonic oscillator and the Kratzer oscillator are extremely poorer than real potential curves. It is again important that the Franck-Condon factors for the Morse potential is expressed as a more analytical formula than Fraser–Jarman method^{5,6} though it is very difficult mathematically to obtain the vibrational overlap integrals of which Franck-Condon factors are proportional to the square.

In the present work, the vibrational overlap integrals for the Morse potential can be presented by analytic functions which are binomial series containing polygamma function and its derivative functions. Using our analytic functions of vibrational overlap integrals, Franck-Condon factors for the electronic transitions: $a^1\Pi_g \leftarrow X^1\Sigma_g^+$, $C^3\Pi_u \leftarrow X^1\Sigma_g^+$ and $b^1\Pi_u \leftarrow X^1\Sigma_g^+$ for N_2 and $A^1\Pi \leftarrow X^1\Sigma^+$ for CO are obtained. In addition Franck-Condon factors for the transitions in ionization processes: $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+ (N_2^+ \text{ and } CO^+) \leftarrow X^1\Sigma^+ (N_2 \text{ and } CO)$ are obtained. Our results are compared with the numerical calculations by RKR analysis^{1–3} and Morse analysis⁴ and the experimental results by the electron energy loss spectra¹² and the photoelectron spectroscopy.¹³

VIBRATIONAL OVERLAP INTEGRALS FOR THE MORSE POTENTIAL

The Morse potential is described by

$$V(r) = -2D \exp[-\alpha(r - r_e)] + D \exp[-2\alpha(r - r_e)] \quad (1)$$

The eigenvalues and eigenfunctions in the discrete states for the Morse potential¹⁴ are given by, respectively,

$$E_n = -D + 2\alpha\hbar(D/2\mu)^{1/2}(n + \frac{1}{2}) - (\alpha^2\hbar^2/2\mu)(n + \frac{1}{2})^2 \quad (2)$$

$$\psi_n(z) = N_n \exp(-z/2) z^{b_n} L_n^{2b_n}(z) \quad (3)$$

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where $N_n = [2\alpha b_n n! / \Gamma(2b_n + n + 1)]^{1/2}$, $z = 2a \exp[-\alpha(r - r_e)]$, $a = \sqrt{2\mu D} / \alpha \hbar$, and $b_n = a - 1/2 - n > 0$.

In the case of the transition from the vibrational quantum number m in the lower electronic state, A , to the vibrational quantum number n in the upper electronic state, B , the six parameters and a variable in state A are defined by μ_A , r_A , α_1 , a_1 , p_m and N_{Am} and z_1 , respectively, and those in state B by μ_B , r_B , α_2 , a_2 , q_n and N_{Bn} and z_2 , respectively, corresponding to μ , r_e , α , a , b_n and N_n and z defined in Eqs. (1), (2) and (3).

Introducing new variable, $z = \sqrt{z_1 z_2} = h \exp[-\alpha(r - r_{AB})]$, where $\alpha = (\alpha_1 + \alpha_2)/2$, $r_{AB} = (r_A + r_B)/2$, and $h = 2\sqrt{a_1 a_2} \exp[(\alpha_1 - \alpha_2)(r_A - r_B)/4]$, then $z_1 = h_1 z^s$ and $z_2 = h_2 z^t$ where $s = \alpha_1/\alpha$, $t = \alpha_2/\alpha$,

$$h_1 = 2a_1 \exp[\alpha_1(r_A - r_B)/2]/h^s, \quad (4)$$

and

$$h_2 = 2a_2 \exp[\alpha_2(r_B - r_A)/2]/h^t. \quad (5)$$

The eigenfunctions in A and B electronic states are given

$$\psi_{Am}(z) = N_{Am} h_1^{p_m} \exp(-h_1/2z^s) z^{sp_m} L_m^{2p_m}(h_1 z^s), \quad (6)$$

and

$$\psi_{Bn}(z) = N_{Bn} h_2^{q_n} \exp(-h_2/2z^t) z^{tq_n} L_n^{2q_n}(h_2 z^t). \quad (7)$$

From Eq. (A11) of the Appendix, vibrational overlap integral, $I(n, m)$, is derived as follows:

$$\begin{aligned} I(n, m) &= \frac{1}{\alpha} \int_0^\infty \psi_{Am}(z_1) \psi_{Bn}(z_2) z^{-1} dz \\ &= \frac{1}{\alpha} N_{Am} N_{Bn} h_1^{p_m} h_2^{q_n} \int_0^\infty e^{-z/2z^{sp_m+tq_n-1}} L_m^{2p_m}(h_1 z^s) L_n^{2q_n}(h_2 z^t) \exp(z - h_1/2z^s - h_2/2z^t) dz \\ &= \frac{2}{\alpha} \left[\frac{\alpha_1 \alpha_2 p_m q_n \Gamma(2p_m + m + 1) \Gamma(2q_n + n + 1)}{m! n!} \right]^{1/2} \frac{\Gamma(sp_m + tq_n)}{\Gamma(2p_m + 1) \Gamma(2q_n + 1)} h_1^{p_m} h_2^{q_n} \\ &\quad \times \sum_{k=0}^\infty \sum_{l=0}^\infty \frac{(-m)_k (-n)_l h_1^k h_2^l}{(2p_m + 1)_k (2q_n + 1)_l k! l!} \frac{\Gamma(sp_m + tq_n + sk + tl)}{\Gamma(sp_m + tq_n)} \\ &\quad \times \exp(U + V + W) F(sp_m + tq_n + sk + tl, s, t, h_1/2, h_2/2), \end{aligned} \quad (8)$$

Table 1. Spectroscopic constants† of N₂, CO, N₂⁺ and CO⁺.

State	ω_e	$\omega_e x_e$	r_e
N ₂ $\mu = 7.001537$			
$X^1\Sigma_g^+$	2358.57	14.324	1.097685
$a^1\Pi_g$	1694.208	13.9491	1.2203
$C^3\Pi_u$	2047.178	28.4450	1.14869
$b^1\Pi_u$	698‡	3.5‡	1.31‡
CO $\mu = 6.8562087$			
$X^1\Sigma^+$	2169.814	13.2883	1.128323
$A^1\Pi$	1518.24	19.40	1.2353
N ₂ $\mu = 7.00140$			
$X^2\Sigma_g^+$	2207.00	16.10	1.11642
$A^2\Pi_u$	1903.70	15.02	1.1749
$B^2\Sigma_u^+$	2419.84	9.29	1.0742
CO ⁺ $\mu = 6.856209$			
$X^2\Sigma^+$	2214.24	15.164	1.11514
$A^2\Pi_i$	1562.06	13.532	1.24377
$B^2\Sigma^+$	1734.18	27.927	1.16877

†Ref. 16.

‡These data are adopted by the reference⁴ since those are vacant in the reference.¹⁶

Table 2. Franck-Condon factors for the $a^1\Pi_g(n) \leftarrow X^1\Sigma_g^+(m)$ transition of N_2 calculated from: (i) present work (uppermost entries), (ii) RKR analysis[†] (middle entries) and (iii) the Morse of Nicholls[‡] (lowermost entries).

$n \backslash m$	0	1	2	3	4	5	6
0	4.270 - 2	1.508 - 1	2.473 - 1	2.497 - 1	1.738 - 1	8.847 - 2	3.411 - 2
	4.315 - 2	1.526 - 1	2.495 - 1	2.502 - 1	1.728 - 1	8.679 - 2	3.306 - 2
	4.315 - 2	1.517 - 1	2.477 - 1	2.492 - 1	1.731 - 1	8.808 - 2	3.399 - 2
1	1.151 - 1	1.930 - 1	8.142 - 2	3.244 - 4	8.670 - 2	1.852 - 1	1.757 - 1
	1.155 - 1	1.931 - 1	7.983 - 2	5.680 - 4	9.050 - 2	1.882 - 1	1.755 - 1
	1.162 - 1	1.932 - 1	8.049 - 2	4.018 - 4	8.732 - 2	1.851 - 1	1.752 - 1
2	1.700 - 1	9.773 - 2	2.956 - 3	1.067 - 1	8.670 - 2	9.590 - 4	6.414 - 2
	1.713 - 1	9.710 - 2	3.407 - 3	1.084 - 1	8.488 - 2	4.928 - 4	6.907 - 2
	1.713 - 1	9.677 - 2	3.276 - 3	1.074 - 1	8.598 - 2	8.554 - 4	6.451 - 2
3	1.827 - 1	1.280 - 2	7.438 - 2	7.017 - 2	3.283 - 3	9.467 - 2	6.621 - 2
	1.830 - 1	1.232 - 2	7.583 - 2	6.864 - 2	4.177 - 3	9.685 - 2	6.357 - 2
	1.835 - 1	1.212 - 2	7.554 - 2	6.931 - 2	3.606 - 3	9.512 - 2	6.580 - 2
4	1.602 - 1	5.815 - 3	9.663 - 2	7.640 - 4	7.668 - 2	3.824 - 2	1.710 - 2
	1.603 - 1	6.199 - 3	9.643 - 2	4.799 - 4	7.834 - 2	3.555 - 2	1.902 - 2
	1.603 - 1	6.391 - 3	9.661 - 2	5.181 - 4	7.744 - 2	3.735 - 2	1.689 - 2
5	1.218 - 1	4.560 - 2	4.773 - 2	3.272 - 2	5.749 - 2	7.624 - 3	8.583 - 2
	1.214 - 1	4.655 - 2	4.658 - 2	3.444 - 2	5.591 - 2	9.399 - 3	7.899 - 2
	1.214 - 1	4.706 - 2	4.668 - 2	3.392 - 2	5.670 - 2	8.364 - 3	7.882 - 2
6	8.355 - 2	8.397 - 2	5.101 - 3	7.221 - 2	3.228 - 3	6.140 - 2	3.253 - 2
	8.287 - 2	8.456 - 2	4.521 - 3	7.273 - 2	2.471 - 3	6.401 - 2	1.323 - 2
	8.287 - 2	8.542 - 2	4.538 - 3	7.289 - 2	2.795 - 3	6.347 - 2	1.485 - 2

[†]Ref. 3.

[‡]Ref. 4.

where

$$\left. \begin{aligned} U &= \exp[\psi(sp_m + tq_n + sk + tl)], \\ V &= -h_1/2 \exp[s\psi(sp_m + tq_n + sk + tl)], \\ W &= -h_2/2 \exp[t\psi(sp_m + tq_n + sk + tl)]. \end{aligned} \right\} \quad (9)$$

and

For $m = 0$, the vibrational overlap integral, $I(n, 0)$, becomes

$$I(n, 0) = \frac{2}{\alpha} \left[\frac{\alpha_1 \alpha_2 p_0 q_n \Gamma(2q_n + n + 1)}{\Gamma(2p_0 + 1)n!} \right]^{1/2} \frac{\Gamma(sp_0 + tq_n)}{\Gamma(2q_n + 1)} h_1^{p_0} h_2^{q_n} \sum_{i=0}^n \frac{(-n)_i h_1^i}{(2q_n + 1)_i i!} \frac{\Gamma(sp_0 + tq_n + tl)}{\Gamma(sp_0 + tq_n)} \times \exp(U + V + W) F(sp_0 + tq_n + tl, s, t, h_1/2, h_2/2), \quad (10)$$

where

$$\left. \begin{aligned} U &= \exp[\psi(sp_0 + tq_n + tl)], \\ V &= -h_1/2 \exp[s\psi(sp_0 + tq_n + tl)], \\ W &= -h_2/2 \exp[t\psi(sp_0 + tq_n + tl)]. \end{aligned} \right\} \quad (11)$$

and

The Franck-Condon factor, $q(n, m)$ is defined as

$$q(n, m) = |I(n, m)|^2. \quad (12)$$

NUMERICAL RESULTS

An experimental energy level is given in terms of spectroscopic data as

$$E_n = -D + \omega_e(n + 1/2) - \omega_e \chi_e(n + 1/2)^2, \quad (13)$$

by comparing Eqs. (2) and (13), we obtain

$$a = \frac{\omega_e}{2\omega_e \chi_e} \quad \text{and} \quad \alpha = \frac{\sqrt{2\mu\omega_e \chi_e}}{\hbar} \quad (14)$$

Table 3. Franck-Condon factors for the $A^1\Pi(n) \leftarrow X^1\Sigma^+(m)$ transition of CO. The entries are arranged as calculated from: (i) present work (upper entries) and the Morse of Nicholls† (lower entries).

$n \backslash m$	0	1	2	3	4	5	6
0	1.105 - 1	2.584 - 1	2.847 - 1	1.978 - 1	9.770 - 2	3.667 - 2	1.090 - 2
	1.132 - 1	2.609 - 1	2.848 - 1	1.763 - 1	9.604 - 2	3.554 - 2	1.034 - 2
1	2.096 - 1	1.571 - 1	4.154 - 3	7.183 - 2	1.900 - 1	1.874 - 1	1.121 - 1
	2.161 - 1	1.549 - 1	3.051 - 3	7.644 - 2	1.931 - 1	1.857 - 1	1.083 - 1
2	2.240 - 1	1.521 - 2	8.370 - 2	1.195 - 1	7.696 - 3	4.965 - 2	1.588 - 1
	2.300 - 1	1.218 - 2	9.013 - 2	1.161 - 1	5.083 - 3	5.718 - 2	1.650 - 1
3	1.791 - 1	1.516 - 2	1.180 - 1	2.211 - 3	8.200 - 2	9.063 - 2	2.338 - 3
	1.813 - 1	2.049 - 2	1.170 - 1	6.454 - 3	8.957 - 2	8.416 - 2	4.713 - 4
4	1.204 - 1	7.579 - 2	4.182 - 2	4.797 - 2	7.392 - 2	2.270 - 3	9.170 - 2
	1.188 - 1	8.729 - 2	3.443 - 2	5.763 - 2	6.656 - 2	6.171 - 3	9.803 - 2
5	7.231 - 2	1.132 - 1	1.833 - 4	8.974 - 2	1.485 - 3	7.524 - 2	3.367 - 2
	6.885 - 2	1.230 - 1	3.236 - 4	9.125 - 2	1.384 - 5	8.236 - 2	2.268 - 2
6	4.031 - 2	1.121 - 1	2.093 - 2	5.168 - 2	3.070 - 2	5.259 - 2	1.046 - 2
	3.668 - 2	1.160 - 1	3.211 - 2	4.220 - 2	4.290 - 2	4.227 - 2	2.178 - 2

†Ref. 4.

From Eq. (14), the parameters of the Morse potential, a , α , and r_e can be determined by using three spectroscopic constants, ω_e , $\omega_e\chi_e$ and r_e and the reduced mass, μ , while the parameters of Rydberg-Klein-Rees potential¹⁵ are determined by the four parameters, ω_e , $\omega_e\chi_e$, B_e and r_e and the reduced mass, μ .

In the present work, Morse Franck-Condon factors are calculated for the electronic transitions in N_2 , CO, $N_2-N_2^+$ and $CO-CO^+$ (Tables 2-6), and are compared with results based upon Morse analysis⁴ and RKR analysis,¹⁻³ and the experimental results by electron energy loss spectroscopy (EELS),¹² and photoelectron spectroscopy (PES).¹³ The spectroscopic constants, ω_e , $\omega_e\chi_e$ and r_e in each electronic state for N_2 , CO, N_2^+ and CO^+ which are required in Tables 2-6 are shown in Table 1. The data of $b^1\Pi_u$ for N_2 are adopted by the reference⁴ while those data are vacant in the reference.¹⁶

Franck-Condon factors compiled 7×7 arrays for N_2 and CO are displayed in Tables 2 and 3. Our results for the Morse potential in Tables 2 and 3 are in good agreement with the results by RKR analysis³ and Morse analysis.⁴ Expanding to 11×11 arrays in Tables 2 and 3, however, Franck-Condon factors for $N_2(a^1\Pi_g \leftarrow X^1\Sigma_g^+)$ in (10, 4), (8-10, 5-7), (4-10, 8), (3-10, 9) and (2-10, 10) corresponding to (n, m) elements are extremely deviated from RKR analysis³ and Morse analysis,⁴ and also those for $CO(A^1\Pi \leftarrow X^1\Sigma^+)$ in (10, 4-5), (9-10, 6), (7-10, 7), (4-10, 8-9) and (4-10, 10) are extremely deviated comparing with Morse analysis.⁴

Table 4. Comparison between calculated and measured Franck-Condon factors for the following transitions: $N_2[a^1\Pi_g(n) \leftarrow X^1\Sigma_g^+(m=0)]$ and $CO[A^1\Pi(n) \leftarrow X^1\Sigma^+(m=0)]$.

n	$N_2(a^1\Pi_g \leftarrow X^1\Sigma_g^+)$				$CO(A^1\Pi \leftarrow X^1\Sigma^+)$		
	Present work	Morse ⁴	RKR ³	EELS ¹²	Present work	Morse ⁴	EELS ¹²
0	0.23	0.24	0.24	0.24	0.49	0.49	0.50
1	0.63	0.63	0.63	0.61	0.94	0.94	0.92
2	0.93	0.93	0.93	0.91	1.00	1.00	1.00
3	1.00	1.00	1.00	1.00	0.80	0.79	0.81
4	0.88	0.87	0.87	0.87	0.54	0.52	0.55
5	0.67	0.66	0.66	0.68	0.32	0.30	0.33
6	0.46	0.45	0.45	0.48	0.18	0.16	0.17
7	0.29	0.29	0.29	0.32	0.096	0.080	0.091
8	0.17	0.17	0.17	0.18	0.049	0.039	0.042
9	0.099	0.096	0.10	0.11	0.025	0.018	0.020
10	0.055	0.053	0.054	0.066	0.013	0.0084	0.0087
11	0.029	0.028	0.028	0.038	0.0063	0.0037	0.0037
12	0.015	0.014	0.015	0.026	0.0032	0.0018	0.0032
13	0.0068	0.0075	0.0085	0.0019	0.0016	0.0008	0.0018
14	0.0013	0.0038	0.0040	0.0012			

Table 5. Comparison between calculated and measured Franck-Condon factors for the following transitions in N_2 : $C^3\Pi_u \leftarrow X^1\Sigma_g^+$ and $b^1\Pi_u \leftarrow X^1\Sigma_g^+$.

n	Present work	Morse†	RKR‡	RKR§	EELS¶
$C^3\Pi_u \leftarrow X^1\Sigma_g^+$					
0	1.00	1.00	1.00	1.00	1.00
2	0.56	0.56	0.54	0.56	0.71
3	0.22	0.19	0.18	0.19	0.37
4	0.072	0.049	0.049	0.054	
$b^1\Pi_u \leftarrow X^1\Sigma_g^+$					
0	0.022	0.017			
1	0.13	0.13			0.18
2	0.38	0.38			0.40
3	0.73	0.73			0.70
4	1.00	1.00			1.00

†Ref. 4.

‡Ref. 2.

§Ref. 3.

¶Ref. 12.

Table 6. Comparison between calculated and measured Franck-Condon factors for the following transitions from $X^1\Sigma^+$ ($m=0$) in N_2 and CO to ionic states (n) in N_2^+ and CO^+ .

State	n	N_2			CO		
		Present work	RKR†	PES†	Present work	RKR†	PES†
$X^2\Sigma^+$	0	1.00	1.00	1.00	1.00	1.00	1.00
	1	0.0853	0.0927	0.0694	0.0380	0.0384	0.0346
	2	0.0051	0.0059	0.0032			
$A^2\Pi$	0	0.828	0.849	0.871	0.369	0.373	0.394
	1	1.00	1.00	1.00	0.819	0.820	0.834
	2	0.690	0.680	0.763	1.00	1.00	1.00
	3	0.361	0.353	0.435	0.893	0.820	0.867
	4	0.160	0.157	0.191	0.653	0.660	0.678
	5	0.0635	0.0637	0.0709	0.417	0.426	0.503
	6	0.0235	0.0243	0.0251	0.241	0.250	0.242
	7	0.0083	0.0089	0.0170	0.129	0.137	0.148
	8	0.0028	0.0032	0.0032	0.0658	0.0715	0.0831
	9				0.0321	0.0359	0.0508
	10				0.0152	0.0175	0.0253
$B^2\Sigma^+$	0	1.00	1.00	1.00	1.00	1.00	1.00
	1	0.131	0.131	0.0984	0.356	0.354	0.350
	2	0.0025	0.0025	0.0076	0.0738	0.0706	0.0775

†Ref. 13.

It is interesting to confront our expressions with the data furnished by electron energy loss spectroscopy and photoelectron spectroscopy since relative Franck-Condon factors, $q(n, 0)$ can be evaluated by those experimental results. In Tables 4–6, we list present work together with the corresponding RKR analysis, Morse analysis and experimental values. Since the experimental data provide only relative peak intensity, it is customary to set the intensity of the highest peak to unity; accordingly, we have also normalized the Franck-Condon factors in the same way. In Tables 4 and 5, our results agree well with RKR analysis³ and Morse analysis⁴ and experimental results by EELS¹² except for the transition for $N_2(C^3\Pi_u \leftarrow X^1\Sigma_g^+)$. Our results for $N_2(C^3\Pi_u \leftarrow X^1\Sigma_g^+)$, however, are consistent with RKR analysis and Morse analysis while the experimental data deviate from three calculated results as shown in Table 5. Agreement among our results, RKR analysis,¹³ Morse analysis⁴ and experimental values by PES¹³ in relative Franck-Condon factors for the ionizing transitions: $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+ \leftarrow X^1\Sigma^+$ is very good as shown in Table 6.

REFERENCES

1. R. N. Zare, *J. Chem. Phys.* **40**, 1934 (1964).
2. R. N. Zare, E. O. Larsson, and R. A. Berg, *J. Molec. Spectrosc.* **15**, 117 (1965).
3. W. Benesch, J. T. Vanderslice, S. T. Tilford, and P. G. Wilkinson, *Astrophys. J.* **143**, 236 (1966).
4. R. W. Nicholls, *JQSRT* **2**, 433 (1962).

5. P. A. Fraser and W. R. Jarman, *Proc. Phys. Soc.* **A56**, 1145 (1953).
6. W. R. Jarman and P. A. Fraser, *Proc. Phys. Soc.* **A56**, 1153 (1953).
7. T. V. Chang and M. Karplus, *J. Chem. Phys.* **52**, 783 (1970).
8. R. W. Nicholls, *J. Chem. Phys.* **74**, 6980 (1981).
9. R. W. Nicholls, *J. Chem. Phys.* **77**, 1614 (1982).
10. S. Waldenström and K. R. Naqvi, *J. Chem. Phys.* **77**, 1613 (1982).
11. S. Waldenström and K. R. Naqvi, *J. Chem. Phys.* **87**, 3563 (1987).
12. E. N. Lassettre, A. Skerbele, M. A. Dillon, and K. J. Ross, *J. Chem. Phys.* **48**, 5066 (1968).
13. J. L. Gardner and A. R. Samson, *J. Chem. Phys.* **60**, 3711 (1974).
14. A. Matsumoto, *J. Phys.* **B21**, 2863 (1988).
15. A. L. G. Rees, *Proc. Phys. Soc. (London)* **59**, 998 (1947).
16. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: IV Constants of Diatomic Molecules*, Van Nostrand-Reinhold, NY (1989).
17. Bateman Manuscript Project, *Higher Transcendental Functions*, p. 44, Vol. 1 and p. 189, Vol. 2, A Erdélyi ed., McGraw-Hill, NY (1953).

APPENDIX

The Laguerre polynomials¹⁷ may be defined by:

$$L_n^\alpha(z) = \frac{\Gamma(\alpha + n + 1)}{\Gamma(\alpha + 1)n!} F(-n, \alpha + 1; z) \quad (\text{A1})$$

where $F(a, b; z)$ is the confluent hypergeometric function. The integral related to the Laguerre polynomials can be obtained as follows:¹⁴

$$\begin{aligned} \int_0^\infty e^{-z} z^{\rho-1} L_m^\alpha(h_1 z^s) L_n^\beta(h_2 z^t) dz \\ = \frac{\Gamma(\alpha + m + 1)\Gamma(\beta + n + 1)}{\Gamma(\alpha + 1)\Gamma(\beta + 1)m!n!} \sum_{k=0}^m \sum_{l=0}^n \frac{(-m)_k (-n)_l h_1^k h_2^l}{(\alpha + 1)_k (\beta + 1)_l k! l!} \Gamma(\rho + sk + tl) \end{aligned} \quad (\text{A2})$$

If $m = 0$, then,

$$\int_0^\infty e^{-z} z^{\rho-1} L_n^\beta(h_2 z^t) dz = \frac{\Gamma(\beta + n + 1)}{\Gamma(\beta + 1)n!} \sum_{l=0}^n \frac{(-n)_l h_2^l}{(\beta + 1)_l l!} \Gamma(\rho + tl) \quad (\text{A3})$$

If $m = 0$ and $n = 0$, then the Eq. (A3) is reduced an integral representation of gamma function:

$$\int_0^\infty e^{-z} z^{\rho-1} dz = \Gamma(\rho). \quad (\text{A4})$$

The integrals of Eq. (18) which integrands contain $\exp(-h_1/2z^s - h_2/2z^t)z^{\rho-1}$ are not easily calculated by expansion into power series of z . Let us attempt that those integrals are expressed as an analytic function by expansion into the series contained polygamma function and its derivative functions. Polygamma function, $\psi(x)$ which is the logarithmic derivative of the gamma function can be defined as follows:¹⁷

$$\psi^{(n)}(x) = \frac{d^{n+1} \log \Gamma(x)}{dx^{n+1}}, \quad n = 0, 1, 2, 3, \quad (\text{A5})$$

where $\psi(x) = \psi^{(0)}(x)$.

First the integral of which the integrand is the integrand of gamma function, $e^{-z}z^{x-1}$, multiplied by z^s is given by

$$\begin{aligned} \int_0^\infty e^{-z} z^{x-1} \exp(s \log z) dz &= \sum_{i=0}^\infty \frac{s^i}{i!} \int_0^\infty e^{-z} z^{x-1} (\log z)^i dz \\ &= \sum_{i=0}^\infty \frac{s^i}{i!} \frac{d^i \Gamma(x)}{dx^i} \\ &= \Gamma(x) \exp(s\psi(x)) [1 + s^2 f_2(x) + s^3 f_3(x) + s^4 f_4(x) + \cdots], \end{aligned} \quad (\text{A6})$$

where

$$\left. \begin{aligned} f_2(x) &= \frac{1}{2!} \psi^{(1)}(x), \\ f_3(x) &= \frac{1}{3!} \psi^{(2)}(x), \\ f_4(x) &= \frac{1}{4!} [3(\psi^{(1)}(x))^2 + \psi^{(3)}(x)]. \end{aligned} \right\} \quad (\text{A7})$$

and

Next, from Eqs. (A6) and (A7), the integral which the integrand is $e^{-z}z^{x-1}$ multiplied by $\exp(z')$ is given by

$$\begin{aligned} \int_0^\infty e^{-z}z^{x-1} \exp(z') dz &= \sum_{i=0}^\infty \frac{1}{i!} \int_0^\infty e^{-z}z^{x-1} \exp(is \log z) dz \\ &= \Gamma(x) \exp(v) [1 + s^2(v + v^2)f_2(x) \\ &\quad + s^3(v + 3v^2 + v^3)f_3(x) + s^4(v + 7v^2 + 6v^3 + v^4)f_4(x) + \dots], \end{aligned} \quad (\text{A8})$$

where $v = \exp(s\psi(x))$.

From Eq. (A8), the integral which the integrand is $e^{-z}z^{x-1}$ multiplied by $\exp(z - az' - bz')$ is obtained by the following

$$\begin{aligned} \int_0^\infty e^{-z}z^{x-1} \exp[z - az' - bz'] dz \\ = \sum_{i=0}^\infty \frac{1}{i!} \sum_{j=0}^\infty \frac{(-a)^j}{j!} \sum_{k=0}^\infty \frac{(-b)^k}{k!} \int_0^\infty e^{-z}z^{x-1} \exp[(i + sj + tk) \log z] dz \\ = \Gamma(x) \exp(U + V + W) F(x, s, t, a, b) \end{aligned} \quad (\text{A9})$$

where $U = \exp(\psi(x))$, $V = -a \exp(s\psi(x))$, $W = -b \exp(t\psi(x))$ and

$$\begin{aligned} F(x, s, t, a, b) &= 1 + [(U + sV + tW)^2 + U + s^2V + t^2W]f_2(x) \\ &\quad + [(U + sV + tW)^3 + 3(U + sV + tW)(U + s^2V + t^2W) + U + s^3V + t^3W]f_3(x) \\ &\quad + [(U + sV + tW)^4 + 6(U + sV + tW)^2(U + s^2V + t^2W) \\ &\quad + 7(U + sV + tW)(U + s^3V + t^3W) + U + s^4V + t^4W - 3stVW(s - t)^2 \\ &\quad - 3U\{(1 - s)^2sV + (1 - t)^2tW\}]f_4(x) + \dots \end{aligned} \quad (\text{A10})$$

From Eqs. (A2), (A9) and (A10), the integral which leads the vibrational overlap integral is expressed as follows:

$$\begin{aligned} \int_0^\infty e^{-z}z^{\rho-1} L_m^\alpha(h_1 z') L_n^\beta(h_2 z') \exp(z - az' - bz') dz &= \frac{\Gamma(\alpha + m + 1) \Gamma(\beta + n + 1) \Gamma(\rho)}{\Gamma(\alpha + 1) \Gamma(\beta + 1) m! n!} \sum_{k=0}^\infty \sum_{l=0}^\infty \\ &\times \frac{(-m)_k (-n)_l h_1^k h_2^l}{(\alpha + 1)_k (\beta + 1)_l k! l!} \frac{\Gamma(\rho + sk + tl)}{\Gamma(\rho)} \exp(U + V + W) F(\rho + sk + tl, s, t, a, b). \end{aligned} \quad (\text{A11})$$