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Unified treatment of Franck–Condon Factors over harmonic oscillator wave function using binomial expansion theorems

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HIGHLIGHTS

- We introduce an alternative analytical formula to calculate the Franck–Condon (FC) factors.
- The main advantage of the base method is its general analytic results.
- The obtained results show a good agreement with the results reported in the literature.

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ABSTRACT

In this article an alternative analytical formula is proposed for Franck–Condon (FC) factors. The proposed method enables us to accurately determine the various level intensities in the spectrum of dia- and polyatomic molecules. This method is based on the use of binomial expansion theorem for the analytical representation of the FC factors. As an example of the effectiveness of the method, we present the calculation results of the FC factors of the molecules AlO, CeO, CrH, CrO, LaO, and NiH. The calculated results are in good agreement with other calculations obtained by theoretical and experimental methods.

1. Introduction

It is well known that the FC principle determines the transition possibility of the electronic state of a molecule with a certain vibration level to the different vibration levels of another electronic state, thereby showing the density distribution of the band spectrum. Since the spectral line intensities and the transition rate are determined by the FC factor, the FC factor plays a critical role in the theory of optical radiationless transitions [1].

The fact that the FC factor provides a quantitative review of the density probability of vibration transition was first proposed in optical spectroscopy. However, understanding the structure of the FC factor is important not only for spectroscopic content but also for the interpretation of polyatomic photo-dissociation, pre-dissociation and reaction dynamics [7–8]. As a result of all these reasons, the FC factor has been a subject of research for a long time, both experimentally and theoretically, for the solution of many problems proposed for direct and indirect calculations [2–29]. Doktorov et al. obtained a general expression using the harmonic oscillator wave function provided by Hermite polynomials. Doktorov et al. have shown that overlap integrals emerge from the FC factor as a matrix element of some operators belonging to a Lie group, and by using this approach, they have obtained recurrence relations for overlap integrals [9]. Cederbaum and Domcke used Boson operators to obtain the repetition correlation of the FC factor [10]. Faulkner, Richardson, and Subbi developed a calculation method of expressing the multi-dimensional FC factor by the mono-dimensional FC factor [11,12]. Using associate Laguerre polynomials and the properties of the harmonic oscillator wave function, Chen and Pei created a formula that can calculate FC overlap integrals [13]. Lermè derived a recurrence relation that included the assumptions of the harmonic approach for the energy curve of attractive potential and Airy function approach for continuous wave function and which could calculate the one- or two-dimensional FC factor [14]. Franck et al. derived a new expression for FC overlap integrals using an algebraic operation based on Bogoliubov transformation [15]. Cho calculated the FC factor in his work using Fermi's golden rule [16]. In more recent times, Kikuchi et al. provided a simple and convenient numerical computer

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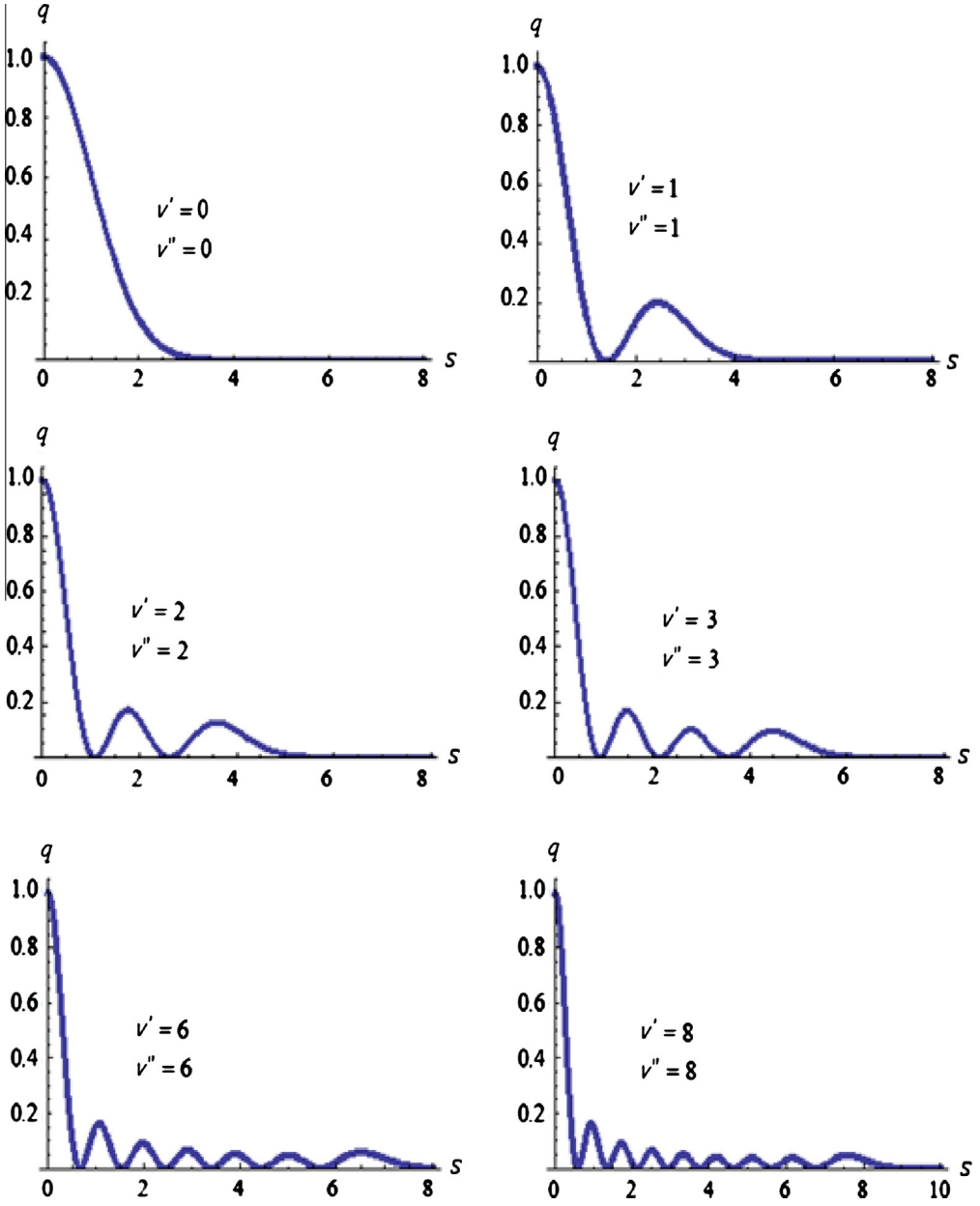

Fig. 1. The dependence $q_{v',v''} = q_{v'',v'}$ upon S for the (0,0), (1,1),...,(8,8) bands in the statements of the equal quantum number ($v' = v''$).

method to calculate FC overlap integrals in polyatomic molecules in spite of the difference in the coordinates of harmonic oscillators and applied this to an SO_2 molecule [17]. In study [22], Nicholls developed efficient formulas for the calculations of FC factor for some values of v' and v''.

The aim of this study is to propose an easily computable analytical formula, as an alternative to the Nicholls' approach, for FC overlap integrals on the basis of the harmonic oscillator wave function. The method suggested is completely general and can be applicable to any polyatomic molecules. The proposed analytical formula includes simple, finite sums, and can be easily calculated for arbitrary values of v' and v''.

2. Analytical evaluation formula for the Franck–Condon Factor

The square of the overlap integral $I_{v',v''}$ is based on the definition of the FC factors defined as

$$q_{v',v''} = |I_{v',v''}|^2. \tag{1}$$

The overlap integral here is defined as

$$I_{v',v''} = \int_{-\infty}^{\infty} \psi_{v'}(x)\psi_{v''}(x')dx, \tag{2}$$

where the functions $\psi_{v'}(x)$ and $\psi_{v''}(x')$ are normalized harmonic oscillator wave functions:

$$\psi_v(x) = N_v H_v(x)\exp(-x^2/2). \tag{3}$$

Here, $x = \frac{r-r_e}{W}$, N_v is the normalization coefficient

$$N_v = \left(\frac{1}{2^v v! W\sqrt{\pi}}\right)^{1/2}, \tag{4}$$

and $H_v(x)$ are the Hermite polynomials [35]

$$H_v(x) = \frac{2^v}{\sqrt{\pi}}\int_{-\infty}^{\infty}(x+it)^v e^{-t^2}dt, \tag{5}$$

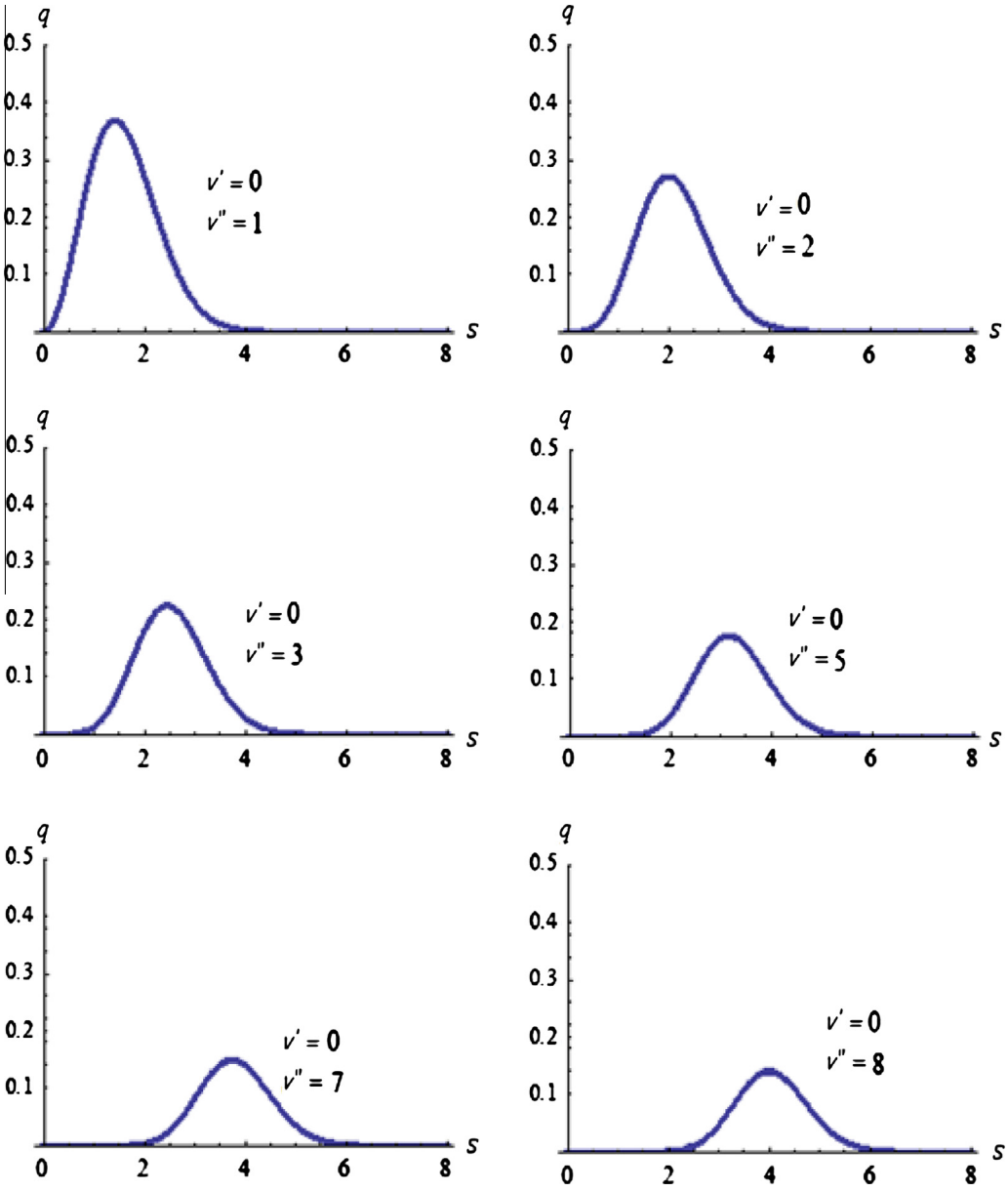

Fig. 2. The dependence $q_{v',v''} = q_{v'',v'}$ upon S for the (0,1), (0,2),…,(0,8) bands in the statements $v' = 0$ (or $v'' = 0$).

where $i = \sqrt{-1}$. In order to establish expressions for the Hermite polynomials, we shall first consider the well-known binomial expansion theorems as follows [30]:

$$(x \pm y)^n = \sum_{m=0}^{\infty} (\pm 1)^m f_m(n) x^{n-m} y^m. \tag{6}$$

Taking into account Eq. (6) in Eq. (5), we obtain the series expansion formulae for the Hermite polynomials in terms of the binomial coefficients and Gamma functions:

$$H_v(x) = \frac{2^{v-1}}{\sqrt{\pi}} \sum_{j=0}^{v} f_j(v) x^{v-j} i^j \Gamma\left(\frac{1+j}{2}\right)[1 + (-1)^j], \tag{7}$$

where $f_m(n) = n!/[m!(n-m)!]$ are the binomial coefficients. Recently, some efficient methods have been developed for FC overlap integrals using the properties of Hermite polynomials [7–8]. The overlap integral $I_{v',v''}$ (Eq. (2)) can be rewritten in the following form [22]:

$$I_{v',v''}(S) = N_{v'} N_{v''} \overline{W} e^{-\frac{S^2}{4}} \int_{-\infty}^{\infty} H_{v'}(\sigma \mp S/2) H_{v''}(\sigma \pm S/2) e^{-\sigma^2} d\sigma, \tag{8}$$

where

$$S = \frac{\Delta r_e}{\overline{W}}, \tag{9}$$

and

$$\sigma = r - \left(\frac{r_{e1} + r_{e2}}{2}\right). \tag{10}$$

Here, $\overline{W}$ is the half-width of the potential at the lowest vibrational level and can be expressed as

$$\overline{W} = \frac{5.807}{\left(\mu_A \tilde{\omega}_e\right)^{1/2}}, \tag{11}$$

where μ_A is the reduced mass, and ω_e is the vibration frequency [22]. Substituting Eq. (11) into Eq. (9), we obtain

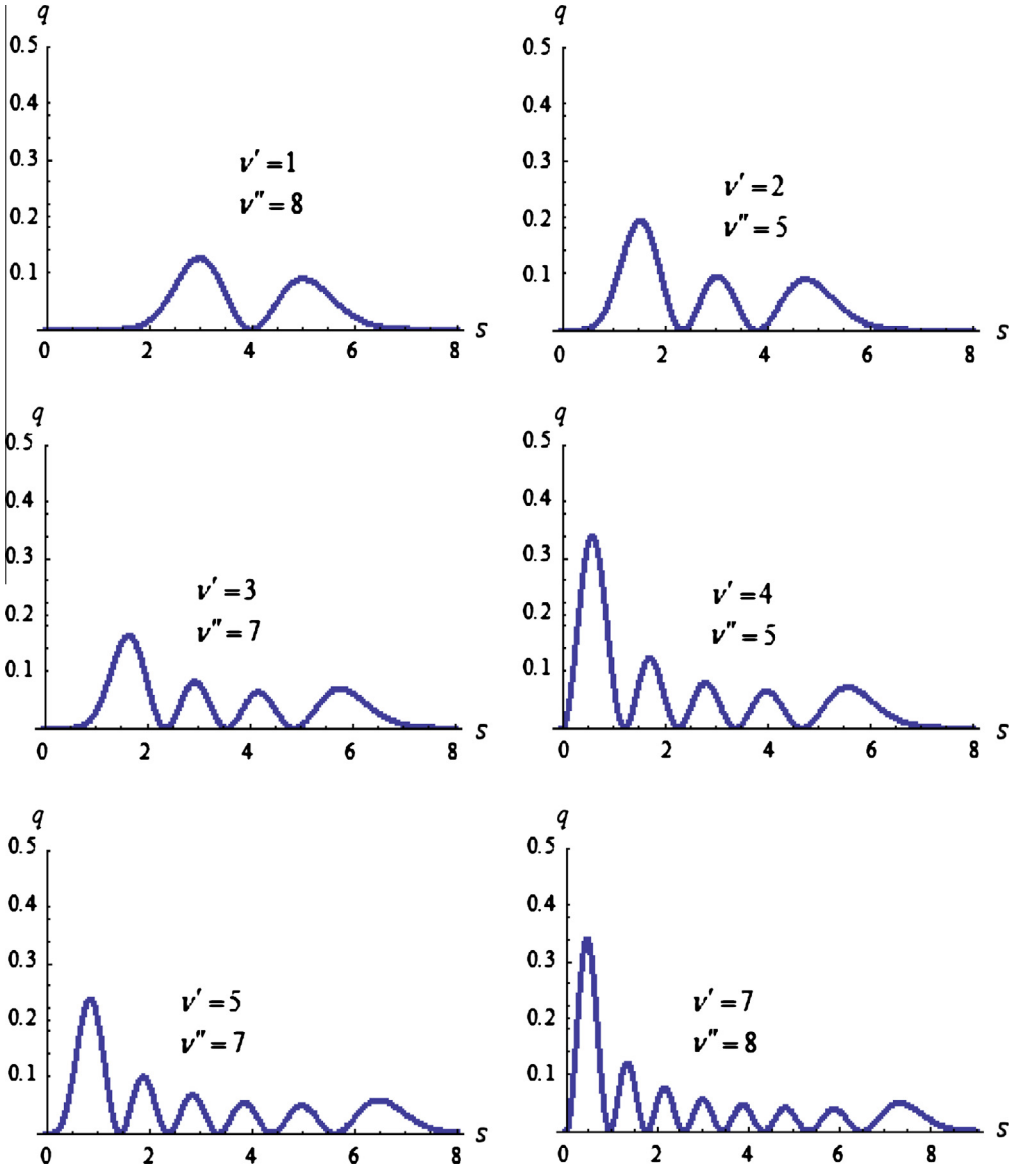

Fig. 3. The dependence $q_{v',v''} = q_{v'',v'}$ upon S for the (1,8), (2,5), (3,7)…. bands in the statements of the different quantum number $(v' \neq v'')$ are given.

$$S = \frac{(\mu_A \tilde{\omega})^{1/2} \Delta r_e}{5.807}. \tag{12}$$

Here, $\tilde{\omega}$ is the average vibration frequency, and r_e is the equilibrium inter-nuclear separation for several electronic states, $\tilde{\omega} = (\omega_{e1} + \omega_{e2})/2$, $\Delta r_e = |r_{e1} - r_{e2}|$, and $r_e \equiv r_{e1}$ or $r_e \equiv r_{e2}$ [22]. Taking into account Eq. (7) in Eq. (8), we obtain the analytical formulae for the overlap integrals over the harmonic oscillator wave function following the form

$$I_{v',v''}(S) = N_{v'} N_{v''} A_{v',v''} \overline{W} e^{-\frac{S^2}{4}} \sum_{k=0}^{v'} \sum_{j=0}^{v''} \sum_{l=0}^{v'-k} \sum_{l'=0}^{v''-j} (-1)^l \left(\frac{S}{2}\right)^{l+l'} i^{k+j} \times f_l(v'-k) f_{l'}(v''-j) f_k(v') f_j(v'') \Gamma\left(\frac{k+1}{2}\right) \Gamma\left(\frac{j+1}{2}\right) \times \Gamma\left(\frac{m}{2}\right) g_{jk}^m \tag{13}$$

where

$$A_{v',v''} = 2^{v'+v''-3}/\pi, \tag{14}$$

$$m = v' + v'' + 1 - j - k - l - l', \tag{15}$$

and

$$g_{jk}^m = [1 + (-1)^j][1 + (-1)^k][1 + (-1)^{m-1}]. \tag{16}$$

In Eq. (13), $\Gamma(\sigma)$ is the Gamma function. As can be seen from Eq. (13), the final formula is expressed in terms of binomial coefficients $F_m(n)$. In order to avoid the calculation of factorials of integers in the formula of binomial coefficients, we use the following recurrence relation:

$$F_m(n) = \left(\frac{n+1}{m} - 1\right) F_{m-1}(n). \tag{17}$$

The Hermitian properties of overlap integrals over the harmonic oscillator wave function and FC factors are determined by

$$I_{v',v''}(S) = I_{v'',v'}(S), \tag{18}$$

$$q_{v',v''}(S) = q_{v'',v'}(S). \tag{19}$$

Table 1
The comparative calculation results FC factors for the AlO ($B^2\Sigma - X^2\Sigma$) band system ($S = 0.814$).

v'/v''	0	1	2	3	4	5	6	7	8
0	7.17991E−01 7.23E−01[a]	2.37869E−01 2.38E−01[a]	3.94028E−02 3.93E−02[a]	4.35135E−03 4.35E−03[a]	3.60399E−04	2.38799E−05	1.31856E−06	6.24051E−08	2.58434E−09
1	2.37869E−01 2.38E−01[a]	3.21059E−01 3.21E−01[a]	3.31181E−01 3.31E−01[a]	9.35418E−02 9.35E−02[a]	1.46416E−02	1.57111E−03	1.27893E−04	8.37691E−06	4.58748E−07
2	3.94028E−02 3.93E−02[a]	3.31181E−01 3.31E−01[a]	1.10489E−01 1.11E−01	3.36796E−01 3.37E−01[a]	1.46906E−01	3.06914E−02	4.10251E−03	3.99169E−04	3.03922E−05
3	4.35135E−03 4.35E−03[a]	9.35418E−02 9.35E−02[a]	3.36796E−01 3.37E−02[a]	1.94723E−02 1.96E−02[a]	2.94577E−01	1.90619E−01	5.12888E−02	8.31742E−03	9.48264E−04
4	3.60399E−04	1.46416E−02	1.46906E−01	2.94577E−01	2.77424E−04	2.31517E−01	2.20473E−01	7.47178E−02	1.44273E−02
5	2.38799E−05	1.57111E−03	3.06914E−02	1.90619E−01	2.31517E−01	1.97436E−02	1.65016E−01	2.35431E−01	9.91238E−02
6	1.31856E−06	1.27893E−04	4.10251E−03	5.12888E−02	2.20473E−01	1.65016E−01	5.56801E−02	1.05465E−01	2.36481E−01
7	6.24051E−08	8.37691E−06	3.99169E−04	8.31742E−03	7.47178E−02	2.35431E−01	1.05465E−01	9.40138E−02	5.82655E−02
8	2.58434E−09	4.58748E−07	3.03922E−05	9.48264E−04	1.44273E−02	9.91238E−02	2.36481E−01	5.82655E−02	1.26550E−01

[a] Ref [22].

Table 2
The comparative calculation results FC factors for the CeO ($B_2 - X_2^3\Phi_3$) band system ($S = 0.512$).

v'/v''	0	1	2	3	4	5	6	7	8
0	8.77155E−01 8.77E−01[a]	1.14970E−01 1.15E−01[a]	7.53470E−03 7.55E−03[a]	3.29196E−04 3.31E−04[a]	1.07871E−05	2.82777E−07	6.17736E−09	1.15668E−10	1.89511E−12
1	1.14970E−01 1.15E−01[a]	6.62283E−01 6.61E−01[a]	2.00789E−01 2.01E−01[a]	2.06721E−02 2.07E−02[a]	1.23190E−03	5.11448E−05	1.62335E−06	4.16374E−08	8.95275E−10
2	7.53470E−03 7.55E−03[a]	2.00789E−01 2.01E−01[a]	4.88734E−01 4.88E−01[a]	2.62139E−01 2.62E−01[a]	3.77709E−02	2.87990E−03	1.45460E−04	5.43541E−06	1.60356E−07
3	3.29196E−04 3.31E−04[a]	2.06721E−02 2.07E−02[a]	2.62139E−01 2.62E−01[a]	3.50555E−01 3.50E−01[a]	3.03137E−01	5.74485E−03	5.38351E−03	3.21689E−04	1.38641E−05
4	1.07871E−05	1.23190E−03	3.77709E−02	3.03137E−01	2.42469E−01	3.27388E−01	7.85514E−02	8.80142E−03	6.09639E−04
5	2.82777E−07	5.11448E−05	2.87990E−03	5.74485E−02	3.27388E−01	1.59817E−01	3.38039E−01	1.00128E−01	1.31495E−02
6	6.17736E−09	1.62335E−06	1.45460E−04	5.38351E−03	7.85514E−02	3.38039E−01	9.84937E−02	3.37825E−01	1.21406E−01
7	1.15668E−10	4.16374E−08	5.43541E−06	3.21689E−04	8.80142E−03	1.00128E−01	3.37825E−01	5.48979E−02	3.29108E−01
8	1.89511E−12	8.95275E−10	1.60356E−07	1.38641E−05	6.09639E−04	1.31495E−02	1.21406E−01	3.29108E−01	2.58799E−02

[a] Ref [22].

Table 3
The comparative calculation results FC factors for the CrH ($A^6\Sigma^+ - X^6\Sigma^+$) band system ($S = 0.880$).

v'/v''	0	1	2	3	4	5	6	7	8
0	6.78955E−01 6.79E−01[a]	2.62891E−01 2.63E−01[a]	5.08958E−02 5.07E−02[a]	6.56895E−03 6.53E−03[a]	6.35874E−04	4.92421E−05	3.17776E−06	1.75775E−07	8.50753E−09
1	2.62891E−01	2.54964E−01 2.56E−01[a]	3.41907E−01	1.15817E−01 1.16E−01[a]	2.14350E−02	2.70602E−03	2.58550E−04	1.98515E−05	1.27338E−06
2	5.08958E−02 5.07E−02[a]	3.41907E−01 3.42E−01[a]	6.13351E−02 6.19E−02[a]	3.20811E−01 3.21E−01[a]	1.73776E−01	4.35145E−02	6.89319E−03	7.90822E−04	7.08037E−05
3	6.56895E−03 6.53E−03[a]	1.15817E−01 1.16E−01[a]	3.20811E−01 3.21E−01[a]	1.95139E−03 2.06E−03[a]	2.54281E−01	2.14581E−01	7.03200E−02	1.36236E−02	1.84035E−03
4	6.35874E−04	2.14350E−02	1.73776E−01	2.54281E−01	1.27047E−02	1.76114E−01	2.35062E−01	9.89004E−02	2.30190E−02
5	4.92421E−05	2.70602E−03	4.35145E−02	2.14581E−01	1.76114E−01	5.26694E−02	1.05492E−01	2.36339E−01	1.26433E−01
6	3.17776E−06	2.58550E−04	6.89319E−03	7.03200E−02	2.35062E−01	1.05492E−01	9.73484E−02	5.16746E−02	2.21865E−01
7	1.75775E−07	1.98515E−05	7.90822E−04	1.36236E−02	9.89004E−02	2.36339E−01	5.16746E−02	1.33569E−01	1.74862E−02
8	8.50753E−09	1.27338E−06	7.08037E−05	1.84035E−03	2.30190E−02	1.26433E−01	2.21865E−01	1.74862E−02	1.55679E−01

[a] Ref [22].

3. Numerical results and discussion

In this study, a new analytical formula is proposed as an alternative to Nicholls' method [22] on a harmonic oscillator basis. Then, using this analytical formula, a new analytical formula that contains the finite sums of the binomial coefficients for the FC overlap integrals on a harmonic oscillator wave function basis is obtained. The binomial coefficients $F_m(n)$ are repeatedly needed in a computation of the two-dimensional FC factors. The algorithm for the storage of coefficients $F_m(n)$ suggested has the important contributions in reducing the requirements for computer time on the calculations [30–34]. Therefore, the proposed formula helps us calculate quickly and precisely the FC factor for arbitrary v' and v''. The series expansions provide an accurate and efficient way to calculate FC factors for the entire permissible range of their parameters.

The calculated results of this study and the results obtained from the literature [22] can be seen in Figs. 1–3 and Tables 1–6. Meanwhile, in Figs. 1–3, the transition of the FC factor $q_{v',v''}(S)$ changes in terms of S transition parameter as given. The results that were obtained for the FC factor on a harmonic oscillator wave function basis from the figures and tables are compared with

Table 4
The comparative calculation results FC factors for the CrO ($B^5\Pi - X^5\Pi$) band system ($S = 1.52$).

v'/v''	0	1	2	3	4	5	6	7	8
0	3.14995E−01	3.63882E−01	2.10178E−01	8.09326E−02	2.33733E−02	5.40017E−03	1.03971E−03	1.71582E−04	2.47765E−05
	3.16E−01[a]	3.64E−01[a]	2.09E−01[a]	8.03E−02[a]					
1	3.63882E−01	7.58729E−03	1.29849E−01	2.38432E−01	1.63745E−01	6.91032E−02	2.11256E−02	5.07405E−03	1.00486E−03
	3.64E−01[a]	7.18E−03[a]	2.39E−01[a]	2.39E−01[a]					
2	2.10178E−01	1.29849E−01	1.30298E−01	4.93182E−02	1.46702E−01	1.93625E−01	1.18921E−01	4.74288E−02	1.40122E−02
	2.09E−01[a]	2.39E−01[a]	1.29E−01[a]	5.35E−03[a]					
3	8.09326E−02	2.38432E−01	4.93182E−02	1.63657E−01	2.45189E−02	4.90261E−02	1.66711E−01	1.53370E−01	7.96259E−02
	8.03E−02[a]	2.39E−01[a]	5.35E−03[a]	1.64E−01[a]					
4	2.33733E−02	1.63745E−01	1.46702E−01	2.45189E−02	1.02654E−02	8.64701E−02	2.67897E−03	1.08685E−01	1.61762E−01
5	5.40017E−03	6.91032E−02	1.93625E−01	4.90261E−02	8.64701E−02	3.20600E−02	1.20411E−01	9.45200E−03	5.00355E−02
6	1.03971E−03	2.11256E−02	1.18921E−01	1.66711E−01	2.67897E−03	1.20411E−01	7.17866E−04	1.10321E−01	4.42732E−02
7	1.71582E−04	5.07405E−03	4.74288E−02	1.53370E−01	1.08685E−01	9.45200E−03	1.10321E−01	1.16967E−02	7.26856E−02
8	2.47765E−05	1.00486E−03	1.40122E−02	7.96259E−02	1.61762E−01	5.00355E−02	4.42732E−02	7.26856E−02	4.43466E−02

[a] Ref [22].

Table 5
The comparative calculation results FC factors for the LaO ($B^2\Sigma^+ - X^2\Sigma^+$) band system ($S = 0.543$).

v'/v''	0	1	2	3	4	5	6	7	8
0	8.62928E−01	1.27217E−01	9.37743E−03	4.60821E−04	1.69841E−05	5.00774E−07	1.23044E−08	2.59138E−10	4.77542E−12
	8.63E−01[a]	1.27E−01[a]	9.37E−03[a]	4.60E−04[a]					
1	1.27217E−01	6.27249E−01	2.18306E−01	2.54353E−02	1.70991E−03	7.99864E−05	2.85880E−06	8.25409E−08	1.99740E−09
	1.27E−01[a]	6.27E−01[a]	2.18E−01[a]	2.54E−02[a]					
2	9.37743E−03	2.18306E−01	4.42407E−01	2.79778E−01	4.59323E−02	3.96317E−03	2.25948E−04	9.51842E−06	3.16367E−07
	9.37E−03[a]	2.18E−01[a]	4.43E−01[a]	2.80E−01[a]					
3	4.60821E−04	2.54353E−02	2.79778E−01	3.00175E−01	3.17260E−01	6.90361E−02	7.34411E−03	4.96273E−04	2.41416E−05
	4.60E−04[a]	2.54E−02[a]	2.80E−01[a]	3.00E−01[a]					
4	0.69841E−05	1.70991E−03	4.59323E−02	3.17260E−01	1.93378E−01	3.35592E−01	9.32220E−02	1.19008E−02	9.34000E−04
5	5.00774E−07	7.99864E−05	3.96317E−03	6.90361E−02	3.35592E−01	1.15787E−01	3.38919E−01	1.17327E−01	1.76205E−02
6	1.23044E−08	2.85880E−06	2.25948E−04	7.34411E−03	9.32220E−02	3.38919E−01	6.20109E−02	3.30764E−01	1.40410E−01
7	2.59138E−10	8.25409E−08	9.51842E−06	4.96273E−04	1.19008E−02	1.17327E−01	3.30764E−01	2.74091E−02	3.14105E−01
8	4.77542E−12	1.99740E−09	3.16367E−07	2.41416E−05	9.34000E−04	1.76205E−02	1.40410E−01	3.14105E−01	8.00589E−03

[a] Ref [22].

Nicholls' results [22] for molecules AlO, CeO, CrH, CrO, LaO, and NiH, and compliance is observed. In this article, the molecular data (the values μ_A, ω_e, and r_e) are given in Table 7. The comparative calculation results of the FC overlap integrals are presented in Table 8. As can be seen, our calculation results are completely in good agreement with Mathematica numerical methods.

Figs. 1–3 show the results obtained for Eq. (1). It is clearly seen from Figs. 1–3 that Eq. (1) has the symmetric property $((v', v'') = (v'', v'))$. In addition, Figs. 1–3 provide the S variation of $q_{v',v''}$. Fig. 1 shows the S variation of $q_{v',v''}$ for the (0,0), (1,1),...,(8,8) bands in statements of the equal quantum number $(v' = v'')$. The S variation of $q_{v',v''}$ for the (0,1), (0,2),...,(0,8) bands in the statements $v' = 0$ (or $v'' = 0$) is shown in Fig. 2. In Fig. 3,

Table 7
Molecules data in this paper, extracted from the compilation of Huber and Herzberg [36].

AlO	$B^2\Sigma$	870.05	1.667	10.0419	0.814
	$X^2\Sigma$	979.23	1.6179		
CeO	B_2	771	1.83958	14.35388	0.512
	$X_2^3\Phi_3$	822.76	1.81175		
CrH	$A^6\Sigma^+$	1479.4	1.787	0.98864	0.880
	$X^6\Sigma^+$	1581.2	1.6557		
CrO	$B^5\Pi$	750.5	1.703	12.229027	1.52
	$X^5\Pi$	898.4	1.615		
LaO	$B^2\Sigma^+$	730.4	1.8557	14.343302	0.543
	$X^2\Sigma^+$	812.75	1.8257		
NiH	$A^2\Delta$	1548.726	1.6458	0.9905931	1.21
	$X^2\Delta$	926.6	1.4756		

Table 6
The comparative calculation results FC factors for the NiH ($A^2\Delta - X^2\Delta$) band system ($S = 1.21$).

v'/v''	0	1	2	3	4	5	6	7	8
0	4.80922E−01	3.52059E−01	1.28862E−01	3.14446E−02	5.75475E−03	8.42553E−04	1.02798E−04	1.07505E−05	9.83740E−07
	4.81E−01[a]	3.52E−01[a]	1.29E−01[a]	3.15E−02[a]					
1	3.52059E−01	3.45289E−02	2.83002E−01	2.20939E−01	8.39531E−02	2.09650E−02	3.89699E−03	5.76952E−04	7.09845E−05
	3.52E−01[a]	3.43E−02[a]	2.343E−01[a]	2.21E−01[a]					
2	1.28862E−01	2.83002E−01	1.85037E−02	1.34810E−01	2.39554E−01	1.37292E−01	4.53780E−02	1.04563E−02	1.84405E−03
	1.29E−01[a]	2.83E−01[a]	1.87E−02[a]	1.34E−01[a]					
3	3.14446E−02	2.20939E−01	1.34810E−01	1.00743E−01	3.31932E−02	2.01451E−01	1.75377E−01	7.55605E−02	2.12491E−02
	3.15E−02[a]	2.21E−01[a]	1.34E−01[a]	1.01E−01[a]					
4	5.75475E−03	8.39531E−02	2.39554E−01	3.31932E−02	1.56294E−01	1.36518E−04	1.37308E−01	1.90444E−01	1.06525E−01
5	8.42553E−04	2.09650E−02	1.37292E−01	2.01451E−01	1.36518E−04	1.59849E−01	1.66376E−02	7.36908E−02	1.82432E−01
6	1.02798E−04	3.89699E−03	4.53780E−02	1.75377E−01	1.37308E−01	1.66376E−02	1.25852E−01	5.48225E−02	2.69826E−02
7	1.07505E−05	5.76952E−04	1.04563E−02	7.55605E−02	1.90444E−01	7.36908E−02	5.48225E−02	7.78625E−02	9.20692E−02
8	9.83740E−07	7.09845E−05	1.84405E−03	2.12491E−02	1.06525E−01	1.82432E−01	2.69826E−02	9.20692E−02	3.50630E−02

[a] Ref [22].

Table 8
The comparative values of the Franck–Condon overlap integrals.

v'	v''	s	Eq. (1)	Mathematica numerical integration results
0	2	0.275	6.88365392719728862171996 4E−04	6.88365392719728862171996 4E−04
7	0	0.417	6.83132184759956611882831 6E−12	6.83132184759956611882831 6E−12
5	3	0.892	4.61387709710694716347565 8E−02	4.61387709710694716347565 8E−02
2	10	1.432	3.00400554205947032533472 8E−04	3.00400554205947032533472 8E−04
6	13	1.846	1.08130117752748962012508 6E−01	1.08130117752748962012508 6E−01
16	1	2.319	1.59814481966460671869274 9E−06	1.59814481966460671869274 9E−06
4	24	3	7.83313997742889529020552 5E−05	7.83313997742889529020552 5E−05
3	32	4	4.12125607881440439755530 0E−06	4.12125607881440439755530 0E−06
1	40	4.169	8.47013645921095445418751 9E−13	8.47013645921095445418751 9E−13
44	3	4.582	1.40182361590443594522364 2E−09	1.40182361590443594522364 2E−09
6	47	1.326	5.25566590568463470347338 7E−46	5.25566590568463470347395 7E−46
3	50	0.753	1.02646461834285873516524 7E−81	1.02646461836869815640356 9E−81
7	58	1.453	7.99328780229280747425558 9E−58	7.99328780469342596064234 1E−58
62	2	1.889	4.13161965476269203616274 0E−65	4.13161965476269204648162 3E−65
70	9	3.326	1.91359243018793632090672 7E−31	1.91359243018793631911106 4E−31

similar to Figs. 1 and 2, the S variations of $q_{v',v''}$ for the (1,8), (2,5), (3,7)... bands in the statements of the different quantum number ($v' \neq v''$) are provided. In addition, every one of the values $q_{v',v''}(S)$ provided in Tables 1–6 has been obtained from the figures. As seen from the obtained results, our results are in excellent agreement with those of Nicholls [22].

We can observe that Nicholls has proposed different formulas for the various values of v' and v''. By increasing v' and v'', high degrees of terms connected to the S transition parameter arise in the obtained formulae. This can cause great challenges in calculations of the FC factor. In this study, with the help of the analytical formula (Eq. (13)) provided for the FC factor, the calculation results given in the tables and figures are similar to those obtained by Nicholls.

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