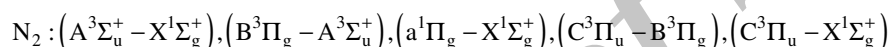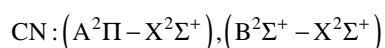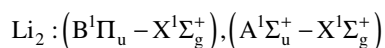# Calculation of Franck-Condon Factors for a Number of Band Systems of Diatomic Molecules Using Hua Potential

Majedifar, Hojat*+; Islampour, Reza

Department of Chemistry, Kharazmi (Tarbiat Moallem) University, Tehran, I.R. IRAN

ABSTRACT: *This work deals with the calculation of Franck-Condon factors using Hua potential function for the first time. The advantages of this function have been mentioned, and the numerical methods are used to obtain Franck-Condon factors for the following band systems:*

$$\text{Li}_2 : \left(B^1\Pi_u - X^1\Sigma_g^+ \right), \left(A^1\Sigma_u^+ - X^1\Sigma_g^+ \right)$$

$$\text{CN} : \left(A^2\Pi - X^2\Sigma^+ \right), \left(B^2\Sigma^+ - X^2\Sigma^+ \right)$$

$$\text{N}_2 : \left(A^3\Sigma_u^+ - X^1\Sigma_g^+ \right), \left(B^3\Pi_g - A^3\Sigma_u^+ \right), \left(a^1\Pi_g - X^1\Sigma_g^+ \right), \left(C^3\Pi_u - B^3\Pi_g \right), \left(C^3\Pi_u - X^1\Sigma_g^+ \right)$$

$$\text{CO} : \left(A^1\Pi - X^1\Sigma \right)$$

Agreement between the values of this work and those obtained from other works is quite good that verifies the reliability of the present calculations.

KEYWORDS: *Franck-Condon factors, Overlap integrals, Potential functions.*

INTRODUCTION

For many problems in molecular spectroscopy, such as study of electronic absorption and emission of a molecular system, preliminary it is necessary to have Franck-Condon factors for transition between vibrational states of upper and lower electronic states of the molecule. In fact, the Franck-Condon factors represent one of the most useful and comprehensive concepts for the study of radiative [1] and non-radiative [2-3] processes in molecular systems.

Intensity of a vibronic transition is controlled by Franck-Condon factor that is defined as the square of the vibrational overlap (or Franck-Condon) integral:

$$q_{v'v''} = \left| \int \psi_{v'} \psi_{v''} \, dR \right|^2 \tag{1}$$

where $\psi_{v'}$ and $\psi_{v''}$ are the vibrational wave functions corresponding to the v' and v'' vibrational levels of the upper and lower electronic states, respectively. Since the molecules vibrate in an anharmonic way, it is necessary to use a potential function, which describes the real movement of the molecules in the best way. We have employed the Hua potential to obtain the vibrational wave functions and have calculated the Franck-Condon factors.

THEORITICAL SECTION

To calculate Franck-Condon factors, one has to evaluate the integral (1) where $\psi_{v'}$ and $\psi_{v''}$ satisfy the time-independent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+U(R)\right]\psi_v = E_v\psi_v \tag{2}$$

The most accurate values of Franck-Condon factors are obtained using the true Rydberg-Klein-Rees (RKR) potential curves. To construct the RKR potential curves we need a set of sufficient spectroscopic data. However, all of the spectroscopic data for all molecules in all their electronic states is not available. In the absence of exact expressions for the vibrational wave function ψ_v one may use the eigenfunctions derived from some approximate potential functions. Consequently, the methods for the calculation of Franck-Condon factors depend on the choice of approximate eigenfunction ψ_v obtained by the solving Schrödinger equation with approximate potential functions.

The various potential functions have been proposed to calculate these factors, such as Morse, which is the most popular empirical potential function because of its simple form [4], *Kratzer* [5], and so on. We use the eigenfunctions of Schrödinger equation for Hua potential function. The details of solving Schrödinger equation for this potential have been brought out comprehensively in reference [6].

Hua potential function has the form:

$$U(R) = D_e\left[\frac{1-e^{-b(R-R_e)}}{1-ce^{-b(R-R_e)}}\right]^2 \tag{3}$$

where $b = a(1-c)$; a , R_e and D_e have the same physical significant as in the Morse potential function and c is an additional constant.

In reference [8], twenty-one empirical potential functions have been compared and fitted to experimental RKR data for ground states of 14 first and second-row diatomic molecules. The functions with more parameters have produced better fits. Hua potential function is the most accurate four-parameter potential that has been examined. This potential has the additional advantage of producing an exactly solvable corresponding Schrödinger equation. Thus, we use this potential function for this work.

In this section, we indicate an alternative way to evaluate anharmonic overlap integrals starting from the wave functions of Hua potential function.

Consider the wave functions of Hua potential [6-7]:

$$\psi_v = N_v\left[\frac{b}{v!}\times\frac{\Gamma\left[2\rho_0(v)+v+1\right]}{\Gamma\left[2\rho_0(v)+v\right]}\times\right. \tag{4}$$

$$\frac{\Gamma\left[2\rho_c+v+1+2\rho_0(v)\right]}{\Gamma\left[2\rho_c+v+1\right]\Gamma\left[2\rho_0(v)\right]}\times\frac{2\rho_c+2v+1+2\rho_0(v)}{2\rho_c+2v+1}\right]^2$$

$$x^{\rho_0(v)}(1-x)^{\rho_c+\frac{1}{2}}F[-v,1+v+2\rho_0(v)+2\rho_c,1+2\rho_c,1+2\rho_0(v);x]$$

where $F[\ldots]$ is the Jacobi Polynomial, $\Gamma[\ldots]$ is the Gamma function,
$N_v = 1$ for $c > 0$, and

$$N_v = \left[\frac{\sin\sin(2\rho_{0(v)}-2\rho)\pi}{\sin\sin(-2\rho\pi)}\right]^{1/2} \quad \text{for} \quad c < 0 \tag{5}$$

$$\rho_0(v) = \frac{\left[t^2(Q-1)-\rho_c\bar{v}-\frac{\bar{v}^2}{2}-1/8\right]}{(\rho_c+\bar{v})} \tag{6}$$

$$t = \frac{2D_e}{\hbar\tilde{\omega}_e(1-c)} \tag{7}$$

$$x = ce^{-b(R-R_e)} \tag{8}$$

$$\tilde{\omega}_e = a\left(\frac{2D_e}{\mu}\right)^{1/2} \tag{9}$$

$$\bar{v} = v+\frac{1}{2} \tag{10}$$

$$\rho_c = \pm\left[\frac{1}{4}+t^2(Q-1)^2\right]^{1/2} \tag{11}$$

$$Q = \frac{1}{c} \tag{12}$$

Here $\tilde{\omega}_e$ is the vibrational frequency in cm^{-1}, and $\pm$ in Eq. (11) refers to the sign of c. Let us denote various quantities in Eq. (4) for two states v' and v'' by a single and a double prime, respectively, and choose x' as the variable in the integral Eq. (1), and in continue omit the prime from x' for simplicity, then we have :

$$dR = -\frac{dx'}{b'x'} = -\frac{dx''}{b''x''}, x'' = hx'^{\gamma} \tag{13}$$

where:

$$h = \frac{c^{''} e^{b^{''}(R_e^{'} - R_e^{''})}}{c^{'\gamma}}, \gamma = \frac{b^{''}}{b^{'}} \qquad (14)$$

Using this variable, the integral in Eq. (1) can be written as:

$$I(v^{'}, v^{''}) = \qquad (15)$$

$$-\frac{N_{v^{'}} N_{v^{''}}}{b^{'}} \int_0^1 \frac{\left(hx^{\gamma}\right)^{\rho_0(v^{'})}}{x} \left[1 - \left(hx^{\gamma}\right)\right]^{\rho^{'}+\frac{1}{2}} x^{\rho_0(v^{''})} (1-x)^{\rho^{''}+\frac{1}{2}}$$

$$F\left[-v^{'}, 1+v^{'}+2\rho_0\left(v^{'}\right)+2\rho^{'}, 1+2\rho_0\left(v^{'}\right); \left(hx^{\gamma}\right)\right] \times$$

$$F\left[-v^{''}, 1+v^{''}+2\rho_0(v^{''})+2\rho^{''}, 1+2\rho_0(v^{''}); x\right] dx$$

for $c > 0$

and

$$I(v^{'}, v^{''}) = \qquad (16)$$

$$-\frac{N_{v^{'}} N_{v^{''}}}{b^{'}} \int_0^{\infty} \frac{\left(hx^{\gamma}\right)^{\rho_0(v^{'})}}{x} \left[1 - \left(hx^{\gamma}\right)\right]^{-\rho^{'}+\frac{1}{2}} x^{\rho_0(v^{'})} (1-x)^{-\rho^{''}+\frac{1}{2}}$$

$$F\left[-v^{'}, 1+v^{'}+2\rho_0\left(v^{'}\right)-2\rho^{'}, 1+2\rho_0\left(v^{'}\right); \left(hx^{\gamma}\right)\right] \times$$

$$F\left[-v^{''}, 1+v^{''}+2\rho_0(v^{''})-2\rho^{''}, 1+2\rho_0(v^{''}); x\right] dx$$

for $c < 0$

Derivation of a closed formula for the overlap integrals Eq. (15) and Eq. (16) is a formidable task. However, the direct integration is simple and can be carried out in a straightforward way.

RESULTS AND DISCUSSION

In this paper we have evaluated the overlap integrals between wave functions belonging to upper and lower electronic transition states involved in transitions for the following systems:
$(B^1\Pi_u - X^1\Sigma_g^+)$ and $(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ of Li_2; $(A^2\Pi\text{-}X^2\Sigma^+)$ and $(B^2\Sigma^+\text{-}X^2\Sigma^+)$ of CN; $(A^3\Sigma_u^+ - X^1\Sigma_g^+)$, $(B^3\Pi_g - A^3\Sigma_u^+)$, $(a^1\Pi_g - X^1\Sigma_g^+)$, $(C^3\Pi_u - B^3\Pi_g)$, and $(C^3\Pi_u - X^1\Sigma_g^+)$ of N_2; $(A^1\Pi - X^1\Sigma)$ of CO.

The computations were performed by a program written in Mathematica codes. The input data for this program is c, D_e, R_e, a, and $\tilde{\omega}_e$ for both states of

the transition involved. The basic molecular spectroscopic data for these transitions is listed in Table 1 and was taken from reference [9] or from original papers of analysis of the band systems. It should be mentioned that no values of adjustable parameter c for $B^1\Pi_u$ and $A^1\Sigma_u^+$ states of Li_2, all states of CN and N_2 and $A^1\Pi$ state of CO have been reported. This parameter has been calculated by minimizing average absolute deviation as described in reference [6].

In common with previous workers, we will use RKR data as "accurate" quantities for the most comparison purposes. The Franck-Condon factors obtained for the band systems of considered molecules are displayed in Tables 2-11.

Franck-Condon factors in this study, have been calculated for transitions between all vibrational levels up to vibrational quantum number 6 or 7 of the respective electronic states except for the $(B^2\Sigma^+\text{-}X^2\Sigma^+)$ system of CN, and are expected to be accurate to three or four decimals. The sums of each row or each column have been calculated. A glimpse to the row and column sums in tables 2-11 reveals significant deviations from unity. This is partly due to the use of Condon approximation in which it is assumed that electronic transition moment is independent of bond length in driving Franck-Condon integral (1) and partly due to the limited range of Δv taken here ; [10].

Tables 2 and 3 present the Franck-Condon factors for two electronic band systems of Li_2. This values indicate that in the $(B^1\Pi_u - X^1\Sigma_g^+)$ system, bands $(v^{'}, v^{''}) \rightarrow (0, 0)$, (0, 1), (1, 0), (2, 0), and in the $(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ system, bands (0, 2), (0, 3), (1, 0), (1, 1), (2, 0), (3, 0), (5, 1) should be relatively intense and all other bands should be comparatively weak.

Tables 4 and 5 contain the Franck-Condon factors for the $(A^2\Pi\text{-}X^2\Sigma^+)$ and $(B^2\Sigma^+\text{-}X^2\Sigma^+)$ systems of CN, respectively. In table 4, bands (0, 0), (0, 1), (1, 0) and (1, 2) are due to the most intense transitions, and bands with $v^{'} \geq 7$ and with $v^{''} \geq 6$ are weakly observed. Table 5 shows that the $\Delta v = 0$ bands are the most intense compare to others, and bands with $v^{'} \geq 4$ and with $v^{''} \geq 3$ which are weakly observed.

Tables 6-10 show the Franck-Condon factors for the $(A^3\Sigma_u^+ - X^1\Sigma_g^+)$, $(B^3\Pi_g - A^3\Sigma_u^+)$, $(a^1\Pi_g - X^1\Sigma_g^+)$, $(C^3\Pi_u - B^3\Pi_g)$, and $(C^3\Pi_u - X^1\Sigma_g^+)$ transitions in N_2 molecule.

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Table 1: Basic molecular data used for the calculation of Franck-Condon Factors.

Molecule	state	c	D_e(cm^{-1})	R_e(A)	a(A^{-1})	$\widetilde{\omega_e}$(cm^{-1})
Li$_2$	X$^1\Sigma_g^+$	-0.14	8541	2.67328	0.867	351.43
	B$^1\Pi_u$	0.1341	8434.5	2.936	0.6698	270.12
	A$^1\Sigma_u^+$	0.0077	8940	3.10821	0.616	255.47
CN	X$^2\Sigma^+$	0.02211	76600	1.17182	2.32	2068.59
	A$^2\Pi$	0.0291	55200	1.2333	2.30	1812.5
	B$^2\Sigma^+$	0.0546	53900	1.15	2.88	2163.9
N$_2$	X$^1\Sigma_g^+$	-0.0561	97089.717	1.097685	2.4575559	2358.57
	a$^1\Pi_g$	-0.0157	51443.117	1.2203	2.4251821	1694.2
	A$^3\Sigma_u^+$	-0.0831	37600	1.28	2.42	1460.64
	B$^3\Pi_g$	-0.0915	51200	1.21	2.46	1733.39
	C$^3\Pi_u$	0.011	36833.695	1.14869	3.4631733	2047.17
CO	X$^1\Sigma$	0.044	88575.905	1.128323	2.3423473	2169.813
	A$^1\Pi$	-0.066	29704.287	1.2353	2.830202	1518.2

Table 2: Franck-Condon Factors for the (B$^1\Pi_u - X^1\Sigma_g^+$) system of Li$_2$.

v′\v″	0	1	2	3	4	5	6	7	Sum
0	0.3226	0.3343	0.1994	0.0905	0.0350	0.0122	0.0040	0.0013	
	0.3188	0.3340	0.2088	0.0918	0.0358	0.0126	0.0042	----------	
	0.3222	0.3154	0.1978	0.0982	----------	----------	----------	----------	0.9993
	0.3382	0.3431	0.1963	0.0828	0.0285	0.0083	0.0021	----------	
1	0.3861	0.0064	0.0983	0.1902	0.1571	0.0905	0.0427	0.0178	
	0.3827	0.0077	0.0942	0.1884	0.1585	0.0929	0.0446	----------	
	0.4090	0.0049	0.0821	0.1688	----------	----------	----------	----------	0.9891
	0.3941	0.0018	0.1255	0.2075	0.1522	0.0760	0.0297	----------	
2	0.2087	0.1619	0.1301	0.0000	0.0773	0.1407	0.1250	0.0798	
	0.2103	0.1511	0.1345	0.0001	0.0711	0.1374	0.1263	----------	
	0.2094	0.1972	0.1143	0.0001	----------	----------	----------	----------	0.9235
	0.2011	0.1966	0.1043	0.0071	0.1181	0.1612	0.1165	----------	
3	0.0667	0.2780	0.1301	0.1559	0.0473	0.0054	0.0728	0.1144	
	0.0698	0.2711	0.0063	0.1508	0.0550	0.0024	0.0631	----------	
	0.0530	0.3117	0.0289	0.1394	----------	----------	----------	----------	0.7518
	0.0565	0.2865	0.0373	0.1564	0.0153	0.0356	0.1220	----------	
4	0.0138	0.1605	0.2056	0.0196	0.0819	0.1038	0.0122	0.0147	
	0.0156	0.1657	0.1834	0.0303	0.0661	0.1082	0.0204	----------	
	----------	----------	----------	----------	----------	----------	----------	----------	0.6121
	0.0092	0.1370	0.2568	0.0005	0.1241	0.0634	0.0013	----------	
5	0.0019	0.0490	0.2267	0.0919	0.0864	0.0138	0.1020	0.0554	
	0.0025	0.0560	0.2243	0.0628	0.1028	0.0039	0.0895	----------	
	----------	----------	----------	----------	----------	----------	----------	----------	0.6271
	0.00085	0.0312	0.2068	0.1765	0.0328	0.0644	0.0949	----------	
6	0.0002	0.0089	0.1012	0.2375	0.0159	0.1235	0.0027	0.0572	
	0.0003	0.0122	0.1149	0.2130	0.0021	0.1224	0.0155	----------	
	----------	----------	----------	----------	----------	----------	----------	----------	0.5471
	0.0000	0.0035	0.0636	0.2497	0.0958	0.0784	0.0190	----------	
7	0.0000	0.0010	0.0240	0.1577	0.1975	0.0017	0.1078	0.0345	
	----------	----------	----------	----------	----------	----------	----------	----------	
	----------	----------	----------	----------	----------	----------	----------	----------	0.5242
	----------	----------	----------	----------	----------	----------	----------	----------	
Sum	1.000	1.000	0.9966	0.9433	0.6984	0.4916	0.4692	0.3751	

First entry: Hua potential, this work, Second entry: RKR values from [11], Third entry: Morse potential from [12],
Forth entry: Morse potential using method of confining the molecule in a spherical box from [13].

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Table 3: Franck-Condon Factors for the $(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ system of Li_2.

v′\v″	0	1	2	3	4	5	6	7	Sum
0	0.0544 0.0520 0.0560	0.1378 0.1340 0.1396	0.1916 0.1870 0.1916	0.1936 0.1900 0.1919	0.1593 0.1570 0.1566	0.1133 0.1130 0.1105	0.0723 0.0730 0.0699	0.0425 ---------- ----------	0.9648
1	0.1834 0.1760 0.1927	0.1990 0.1970 0.1983	0.0763 0.0790 0.0704	0.0025 0.0030 0.0012	0.0208 0.0180 0.0243	0.0723 0.0680 0.0760	0.1050 0.1020 0.1060	0.1066 ---------- ----------	0.7659
2	0.2808 0.2700 0.2926	0.0537 0.0580 0.0440	0.0186 0.0150 0.0260	0.1013 0.0980 0.1062	0.0875 0.0900 0.0807	0.0237 0.0270 0.0172	0.0003 ---------- 0.0016	0.0247 ---------- ----------	0.5906
3	0.2560 0.2500 0.2555	0.0143 0.0090 0.0265	0.1313 0.1270 0.1349	0.0388 0.0450 0.0266	0.0063 0.0040 0.0134	0.0644 0.0600 0.0723	0.0749 ---------- 0.0687	0.0326 ---------- ----------	0.6186
4	0.1532 0.1560 0.1403	0.1533 0.1340 0.1851	0.0469 0.0560 0.0284	0.0332 0.0250 0.0529	0.0922 0.0920 0.0877	0.0238 0.0300 0.0115	0.0050 0.0020 0.0138	0.0489 ---------- ----------	0.5565
5	0.0626 0.0680 0.0498	0.2230 0.2110 0.2285	0.0171 0.0080 0.0443	0.1121 0.1120 0.1025	0.0034 0.0090 0.0002	0.0481 0.0390 0.0668	0.0675 0.0710 0.0551	0.0127 ---------- ----------	0.5465
6	0.0176 0.0210 0.1132	0.1529 0.1590 0.1302	0.1601 0.1290 0.2046	0.0124 0.0250 0.0001	0.0768 0.0610 0.1011	0.0500 0.0620 0.0251	0.0000 0.0020 0.0175	0.0547 ---------- ----------	0.5245
Sum	1.008	0.9340	0.6418	0.4939	0.4463	0.3956	0.3250	0.3227	

First entry: Hua potential, this work, Second entry: RKR values from [14],
Third entry: Morse potential using method of confining the molecule in a spherical box from [13].

Table 4: Franck-Condon Factors for the $(A^2\Pi - X^2\Sigma^+)$ system of CN.

v′\v″	0	1	2	3	4	5	6	7	Sum
0	0.5004 0.4940 0.5047	0.3578 0.3600 0.3551	0.1163 0.1190 0.1149	0.0225 0.0234 0.0223	0.0028 ---------- ----------	0.0003 ---------- ----------	0.0000 ---------- ----------	0.0000 ---------- ----------	1.0001
1	0.3291 0.3350 0.3295	0.0444 0.0426 0.0476	0.3201 0.3180 0.3201	0.2242 0.2220 0.2215	0.0687 ---------- ----------	0.0121 ---------- ----------	0.0014 ---------- ----------	0.0001 ---------- ----------	1.0001
2	0.1242 0.1260 0.1222	0.2579 0.2640 0.2638	0.0148 0.0137 0.0127	0.1701 0.1740 0.1728	0.2706 ---------- ----------	0.1274 ---------- ----------	0.0304 ---------- ----------	0.0043 ---------- ----------	0.9997
3	0.0355 0.0349 0.0339	0.2054 0.2070 0.2053	0.1082 0.1200 0.1157	0.0988 0.0925 0.0943	0.0487 ---------- ----------	0.2506 ---------- ----------	0.1830 ---------- ----------	0.0582 ---------- ----------	0.9884
4	0.0086 ---------- ----------	0.0923 ---------- ----------	0.2029 ---------- ----------	0.0158 ---------- ----------	0.1549 ---------- ----------	0.0010 ---------- ----------	0.1861 ---------- ----------	0.2211 ---------- ----------	0.8827
5	0.0018 ---------- ----------	0.0309 ---------- ----------	0.1413 ---------- ----------	0.1418 ---------- ----------	0.0034 ---------- ----------	0.1487 ---------- ----------	0.0167 ---------- ----------	0.1075 ---------- ----------	0.5921
6	0.0004 ---------- ----------	0.0086 ---------- ----------	0.0643 ---------- ----------	0.1603 ---------- ----------	0.0672 ---------- ----------	0.0405 ---------- ----------	0.0996 ---------- ----------	0.0626 ---------- ----------	0.5035
7	0.0001 ---------- ----------	0.0021 ---------- ----------	0.0228 ---------- ----------	0.0989 ---------- ----------	0.1436 ---------- ----------	0.0150 ---------- ----------	0.0852 ---------- ----------	0.0430 ---------- ----------	0.4107
Sum	1.0001	0.9994	0.9907	0.9324	0.7599	0.5956	0.6024	0.4968	

First entry: Hua potential, this work, Second entry: Kratzer potential from [15],
Third entry: Morse potential using method of confining the molecule in a spherical box from [13].

Table 5: Franck-Condon Factors for the ($B^2\Sigma^+$-$X^2\Sigma^+$) system of CN.

v´\v″	0	1	2	3	4	Sum
0	0.9174 0.9067 0.9118 0.9201	0.0757 0.0484 0.0818 0.0742	0.0065 0.0335 0.0060 0.0054	0.0004 0.0070 0.0004 0.0003	0.0000 --------- --------- ---------	1.0000
1	0.0818 0.0782 0.0860 0.0788	0.7833 0.7719 0.7512 0.0786	0.1183 0.4442 0.1449 0.1206	0.0152 0.0731 0.0165 0.0132	0.0013 --------- --------- 0.0009	0.9999
2	0.0008 0.0132 0.0022 0.0011	0.1394 0.1309 0.1605 0.1369	0.6943 0.6666 0.6120 0.6910	0.1391 0.0231 0.1916 0.1474	0.0237 --------- --------- 0.0216	0.9973
3	0.0000 0.0011 0.0000 ---------	0.0014 0.0426 0.0065 0.0024	0.1791 0.1519 0.2243 0.1795	0.6388 0.5762 0.4426 0.6252	0.1453 --------- --------- 0.1603	0.9646
4	0.0000 --------- --------- ---------	0.0002 --------- --------- ---------	0.0014 --------- --------- 0.0032	0.2047 --------- --------- 0.2101	0.6095 --------- --------- 0.5827	0.8158
Sum	1.0000	1.0000	0.9996	0.9982	0.7798	

First entry: Hua potential, this work, Second entry: Morse potential from [16],
Third entry: Morse potential with anharmonic corrections from [17],
Forth entry: by asymptotic expansion method of Chang and Karplus from [18].

Table 6: Franck-Condon Factors for the ($A^3\Sigma_u^+ - X^1\Sigma_g^+$) system of N_2.

v´\v″	0	1	2	3	4	5	6	Sum
0	0.0016 0.0011 0.0015	0.0082 0.0056 0.0075	0.0228 0.0157 0.0205	0.0449 0.0315 0.0398	0.0700 0.0507 0.0618	0.0922 ---------- ----------	0.1067 ---------- ----------	0.3464
1	0.0114 0.0084 0.0112	0.0434 0.0327 0.0417	0.0848 0.0665 0.0801	0.1091 0.0931 0.1040	0.1035 0.0991 0.1020	0.0731 ---------- ----------	0.0360 ---------- ----------	0.4613
2	0.0403 0.0334 0.0408	0.1021 0.0888 0.1010	0.1187 0.1150 0.1180	0.0756 0.0891 0.0782	0.0208 0.0400 0.0253	0.0000 ---------- ----------	0.0162 ---------- ----------	0.3737
3	0.0914 0.0829 0.0938	0.1340 0.1330 0.1350	0.0655 0.0812 0.0670	0.0034 0.0135 0.0046	0.0160 0.0036 0.0124	0.0482 ---------- ----------	0.0577 ---------- ----------	0.4162
4	0.1489 0.1440 0.1530	0.0974 0.1090 0.0971	0.0025 0.0094 0.0028	0.0334 0.0174 0.0300	0.0677 0.0605 0.0668	0.0371 ---------- ----------	0.0021 ---------- ----------	0.3891
5	0.1852 0.1890 0.1900	0.0272 0.0367 0.0253	0.0277 0.0177 0.0288	0.0769 0.0736 0.0758	0.0253 0.0388 0.0262	0.0018 ---------- ----------	0.0365 ---------- ----------	0.3806
6	0.1828 0.1920 0.1850	0.0009 0.0001 0.0018	0.0838 0.0813 0.0869	0.0293 0.0421 0.0303	0.0074 0.0011 0.0060	0.0543 ---------- ----------	0.0360 ---------- ----------	0.3945
Sum	0.6616	0.4132	0.4058	0.3726	0.3107	0.3067	0.2912	

First entry: Hua potential, this work, Second entry: RKR values from [19],
Third entry: Morse potential using method of confining the molecule in a spherical box from [13].

Table 7: Franck-Condon Factors for the $(B^3\Pi_g - A^3\Sigma_u^+)$ system of N_2.

v'\v''	0	1	2	3	4	5	6	Sum
0	0.4392	0.3147	0.1338	0.0310	0.0033	0.0021	0.0000	
	0.4100	0.3310	0.1660	0.0669	---------	---------	---------	0.9241
	0.4400	0.3280	0.1500	0.0556	0.0184	0.0056	0.0017	
	0.3410	0.3230	0.1900	0.0880	0.0360	0.0140	0.0050	
1	0.3790	0.0139	0.1648	0.1414	0.0547	0.0458	0.0000	
	0.3980	0.0029	0.1590	0.1970	---------	---------	---------	0.7996
	0.3910	0.0139	0.1920	0.1990	0.1170	0.0537	0.0214	
	0.4060	0.0020	0.1030	0.1770	0.1450	0.0890	0.0420	
2	0.1374	0.2910	0.0321	0.0387	0.0916	0.0868	0.1094	
	0.1620	0.2740	0.0688	0.0221	---------	---------	---------	0.7870
	0.1400	0.3110	0.0426	0.0462	0.1490	0.1430	0.0895	
	0.2000	0.2120	0.1130	0.0020	0.0740	0.1260	0.1190	
3	0.0286	0.2339	0.1262	0.0703	0.0199	0.0557	0.0414	
	0.0342	0.2760	0.0956	0.1520	---------	---------	---------	0.5760
	0.0259	0.2580	0.1420	0.1320	0.0000	0.0700	0.1250	
	0.0500	0.3010	0.0390	0.1610	0.0310	0.0090	0.0690	
4	0.0034	0.0847	0.2838	0.0224	0.1049	0.0265	0.0040	
	---------	---------	---------	---------	---------	---------	---------	0.5297
	0.0026	0.0771	0.3020	0.0293	0.1600	0.0274	0.0145	
	0.0060	0.1340	0.2730	0.0010	0.1130	0.0860	0.0040	
5	0.0002	0.0228	0.1368	0.1986	0.0051	0.0405	0.0834	
	---------	---------	---------	---------	---------	---------	---------	0.4874
	0.0001	0.0111	0.1410	0.2760	0.0002	0.1270	0.0741	
	0.0000	0.0270	0.2100	0.1840	0.0460	0.0440	0.1040	
6	0.0000	0.0010	0.0241	0.1779	0.0888	0.0060	0.0468	
	---------	---------	---------	---------	---------	---------	---------	0.3446
	0.0000	0.0008	0.0275	0.2030	0.2070	0.0284	0.0689	
	0.0000	0.0030	0.0590	0.2590	0.0830	0.1070	0.0030	
Sum	0.9878	0.9620	0.9016	0.6803	0.3683	0.2634	0.2850	

First entry: Hua potential, this work, Second entry: kratzer potential from [15],

Third entry: Morse potential using method of confining the molecule in a spherical box from [13], Forth entry: from [20].

Table 8: Franck-Condon Factors for the $(a^1\Pi_g - X^1\Sigma_g^+)$ system of N_2.

v'\v''	0	1	2	3	4	5	6	Sum
0	0.0403	0.1111	0.1671	0.1823	0.1616	0.1240	0.0857	
	0.0431	0.1162	0.1713	0.1835	0.1603	0.1214	0.0828	0.8721
	0.0406	0.1112	0.1663	0.1809	0.1606	0.1237	0.0858	
	0.0427	0.1151	0.1700	0.1827	0.1602	0.1218	0.0835	
1	0.1435	0.1923	0.1022	0.0155	0.0045	0.0425	0.0812	
	0.1517	0.1932	0.0967	0.0121	0.0063	0.0470	0.0854	0.5817
	0.1463	0.1922	0.1016	0.0153	0.0041	0.0414	0.0802	
	0.1508	0.1930	0.0977	0.0128	0.0058	0.0456	0.0839	
2	0.2391	0.0902	0.0013	0.0685	0.0975	0.0520	0.0071	
	0.2477	0.0804	0.0032	0.0755	0.0966	0.0466	0.0045	0.5557
	0.2440	0.0859	0.0017	0.0698	0.0968	0.0513	0.0070	
	0.2473	0.0814	0.0029	0.0743	0.0096	0.0477	0.0051	
3	0.2477	0.0000	0.0992	0.0759	0.0023	0.0273	0.0700	
	0.2492	0.0004	0.1074	0.0693	0.0005	0.0339	0.0728	0.5224
	0.2504	0.0000	0.1028	0.0739	0.0017	0.0285	0.0701	
	0.2497	0.0003	0.1067	0.0701	0.0007	0.0327	0.0722	
4	0.1787	0.0674	0.0937	0.0009	0.0630	0.0625	0.0062	
	0.1731	0.0873	0.0859	0.0036	0.0774	0.0567	0.0027	0.4724
	0.1771	0.0809	0.0906	0.0018	0.0731	0.0607	0.0050	
	0.1738	0.0867	0.0867	0.0032	0.0766	0.0574	0.0032	
5	0.0953	0.1663	0.0041	0.0854	0.0469	0.0034	0.0572	
	0.0880	0.1851	0.0008	0.0951	0.0373	0.0083	0.0634	0.4586
	0.0916	0.1823	0.0020	0.0910	0.0424	0.0053	0.0597	
	0.0884	0.1852	0.0009	0.0946	0.0382	0.0076	0.0614	
6	0.0390	0.1778	0.0500	0.0764	0.0084	0.0767	0.0233	
	0.0339	0.1752	0.0645	0.0658	0.0168	0.0788	0.0148	0.4516
	0.0358	0.1779	0.0584	0.0707	0.0127	0.0783	0.0191	
	0.0341	0.1757	0.0641	0.0662	0.0171	0.0858	0.0325	
Sum	0.9836	0.8051	0.5176	0.5049	0.3842	0.3884	0.3307	

First entry: Hua potential, this work, Second entry: Morse potential from [22],

Third entry: Morse potential using method of confining the molecule in a spherical box from [13], Forth entry: Morse potential from [21].

Table 9: Franck-Condon Factors for the $(C^3\Pi_u - B^3\Pi_g)$ system of N_2.

v´\v˝	0	1	2	3	4	5	6	Sum
0	0.5024	0.3801	0.1058	0.0114	0.0003	0.0000	0.0000	1.0000
	0.4550	0.3880	0.1340	0.0216	0.0012	----------------	----------------	
	0.4980	0.3820	0.1080	0.0122	0.0004	----	--------------	
	0.4493	0.3899	0.1349	0.0236	0.0022	0.0001		
1	0.3242	0.0605	0.3814	0.2039	0.0293	0.0007	0.0000	1.0000
	0.3310	0.0229	0.3350	0.2520	0.0566	----------------	----------------	
	0.3220	0.0541	0.3790	0.2110	0.0330	----	----	
	0.3287	0.0187	0.3223	0.2515	0.0696	0.0088	0.0005	
2	0.1259	0.2533	0.0007	0.2974	0.2741	0.0477	0.0009	1.0000
	0.1450	0.2120	0.0230	0.2040	0.3260	----------------	----------------	
	0.1280	0.2430	0.0026	0.2830	0.2850	----	----	
	0.1469	0.2038	0.0330	0.1630	0.1273	0.0211	0.0015	
3	0.0369	0.1902	0.1387	0.0318	0.2176	0.3216	0.0624	0.9992
	0.0494	0.2020	0.0691	0.0881	0.1130	----------------	----------------	
	0.0396	0.1900	0.1210	0.0455	0.1900	----	----	
	0.0523	0.2003	0.0596	0.1181	0.0475	0.2942	0.1852	
4	0.0087	0.0826	0.1927	0.0606	0.0667	0.1617	0.3557	0.9287
	0.0145	0.1090	0.1690	0.0065	0.1160	----------------	----------------	
	0.0103	0.0884	0.1850	0.0420	0.0885	----	----	
	0.0163	0.1124	0.1614	0.0018	0.1570	0.0020	0.2449	
5	0.0017	0.0259	0.1171	0.1644	0.0204	0.0867	0.1286	0.5448
	0.0039	0.0443	0.1410	0.1020	0.0025	----------------	----------------	
	0.0023	0.0309	0.1230	0.1460	0.0074	----	----	
	0.0047	0.0484	0.1427	0.0889	0.0142	0.1411	0.0098	
6	0.0002	0.0062	0.0467	0.1347	0.1282	0.0042	0.0927	0.4129
	0.0010	0.0152	0.0772	0.1370	0.0470	----------------	----------------	
	0.0005	0.0088	0.0553	0.1360	0.1010	----	----	
	0.0013	0.0179	0.0830	0.1345	0.0294	0.0536	0.0962	
Sum	1.0000	0.9988	0.9831	0.9042	0.7366	0.6226	0.6403	

First entry: Hua potential, this work, Second entry: RKR values from [19],

Third entry: Morse potential using method of confining the molecule in a spherical box from [13],

Forth entry: by asymptotic expansion method of Chang and Karplus from [18].

Table 10: Franck-Condon Factors for the $(C^3\Pi_u - X^1\Sigma_g^+)$ system of N_2.

v´\v˝	0	1	2	3	4	5	6	Sum
0	0.5169	0.3043	0.1179	0.0402	0.0134	0.0046	0.0017	0.9990
	0.5210	0.3040	0.1170	0.0393	0.0129	----------------	----------------	
	0.5590	0.3030	0.1010	0.0276	0.0071	----	----	
1	0.3597	0.0476	0.2273	0.1859	0.0991	0.0452	0.0197	0.9845
	0.3600	0.0520	0.2310	0.1850	0.0968	----------------	----------------	
	0.3360	0.0873	0.2710	0.1820	0.0788	----	----	
2	0.1032	0.3452	0.0221	0.0687	0.1535	0.1318	0.0822	0.9067
	0.1010	0.3530	0.0177	0.0761	0.1580	----------------	----------------	
	0.0903	0.3640	0.0018	0.1300	0.1820	----	----	
3	0.0177	0.2240	0.1713	0.1305	0.0002	0.0668	0.1122	0.7227
	0.0164	0.2200	0.1870	0.1210	0.0013	----------------	----------------	
	0.0133	0.1950	0.2440	0.0711	0.0242	----	----	
4	0.0023	0.0648	0.2811	0.0285	0.1745	0.0400	0.0054	0.5966
	0.0019	0.0599	0.2840	0.0401	0.1740	----------------	----------------	
	0.0011	0.0447	0.2670	0.0992	0.1480	----	----	
5	0.0002	0.0122	0.1352	0.2394	0.0063	0.1147	0.1066	0.6146
	0.0001	0.0103	0.1270	0.2560	0.0016	----------------	----------------	
	0.0000	0.0058	0.0952	0.2800	0.0094	----	----	
6	0.0000	0.0017	0.0369	0.2012	0.1302	0.0740	0.0276	0.4716
	0.0000	0.0013	0.0315	0.1940	0.1570	----------------	----------------	
	0.0000	0.0005	0.0180	0.1580	0.2190	----	----	
Sum	1.0000	0.9998	0.9918	0.8944	0.5772	0.4771	0.3554	

First entry: Hua potential, this work,

Second entry: Morse potential using method of confining the molecule in a spherical box from [13], Third entry: from [19].

Table 11: Franck-Condon Factors for the $(A^1\Pi - X^1\Sigma)$ system of CO.

v'\v''	0	1	2	3	4	5	6	Sum
0	0.1104 0.1132 0.1105 0.1069	0.2594 0.2609 0.2584 0.2053	0.2868 0.2848 0.2847 0.2222	0.1986 0.1763 0.1978 0.1800	0.0967 0.0960 0.0977 0.1225	0.0353 0.0355 0.0367 0.0745	0.0100 0.0103 0.0109 0.0420	0.9972
1	0.2132 0.2161 0.2096 0.2542	0.1571 0.1549 0.1571 0.1602	0.0036 0.0031 0.0042 0.0177	0.0762 0.0764 0.0718 0.0126	0.1954 0.1931 0.1900 0.0713	0.1872 0.1857 0.1874 0.1103	0.1076 0.1083 0.1121 0.1116	0.9403
2	0.2293 0.2300 0.2240 0.2846	0.0135 0.0122 0.0152 0.0056	0.0881 0.0901 0.0837 0.0790	0.1167 0.1161 0.1195 0.1185	0.0050 0.0051 0.0077 0.0454	0.0595 0.0572 0.0497 0.0007	0.1689 0.1650 0.1588 0.0178	0.6810
3	0.1826 0.1813 0.1791 0.2007	0.0189 0.0205 0.0152 0.0669	0.1169 0.1170 0.1180 0.1217	0.0008 0.0065 0.0022 0.0035	0.0897 0.0896 0.0820 0.0437	0.0835 0.0842 0.0906 0.0888	0.0002 0.0005 0.0023 0.0548	0.4926
4	0.1206 0.1181 0.1204 0.1005	0.0851 0.0873 0.0758 0.1870	0.0354 0.0344 0.0418 0.0098	0.0563 0.0576 0.0480 0.0777	0.0663 0.0666 0.0739 0.0769	0.0066 0.0062 0.0023 0.0027	0.0993 0.0980 0.0917 0.0269	0.4696
5	0.0704 0.0689 0.0723 0.0382	0.1221 0.1230 0.1132 0.1890	0.0002 0.0003 0.0002 0.0452	0.0903 0.0913 0.0897 0.0937	0.0000 0.0000 0.0015 0.0012	0.0821 0.0824 0.0752 0.0723	0.0215 0.0227 0.0337 0.0560	0.3866
6	0.0376 0.0369 0.0403 0.0115	0.1164 0.1160 0.1121 0.1151	0.0311 0.0321 0.0209 0.1555	0.0422 0.0422 0.0517 0.0037	0.0420 0.0429 0.0307 0.0885	0.0415 0.0423 0.0526 0.0369	0.0225 0.0218 0.0105 0.0086	0.3333
Sum	0.9641	0.7725	0.5621	0.5811	0.4951	0.4957	0.4300	

First entry: Hua potential, this work, Second entry: Morse potential from [22], Third entry: Morse potential from [21],
Forth entry: Morse potential using method of confining the molecule in a spherical box from [13].

From Table 6 it can be seen that all values are fairly small; nevertheless, only bands (2, 2), (3, 1), (4, 0), (5, 0), and (6, 0) are rather intense compare with other values.

From the values of the Franck-Condon factors in table 7 we see that bands (0, 0), (0, 1), (1, 0), and (2, 1) are intense compare with other bands, and bands with $v' \geq 6$ and $v'' \geq 6$ may appear weakly in the spectra.

Careful inspection of table 8 reveals that for some bands, the Franck-Condon factors are small; however, in comparison to other bands the following bands are fairly intense:

(0, 2), (0, 3), (0, 4), (1, 0), (1, 1), (2, 0), (3, 0), (3, 4), (4, 0), (5, 1), and (6, 1).

It can be seen from the magnitude of Franck-Condon factors of $(C^3\Pi_u - B^3\Pi_g)$ system of N_2 given in Table 9 that bands (0, 0), (0, 1), (1, 0), and (1, 2) are the strongest and bands with $v' \geq 6$ and $v'' \geq 5$ are probably weak.

Table 10 shows that there are a diminishing order in values of the Franck-Condon factors in $(C^3\Pi_u - X^1\Sigma_g^+)$ system of N_2. Some values are substantially large,

for example, in bands (0, 0), (0, 1), (1, 0), and (2, 1). Franck-Condon factors of successive bands decline rapidly, as v' and v'' increase.

Finally the values of the Franck-Condon factors calculated for $(A^1\Pi - X^1\Sigma)$ system of CO have been tabulated in table 11. These values for the following band systems are rather large in comparison with the others:
(1, 1), (0, 2), (0, 3), (1, 0), (1, 4), (1, 5), (2, 0), and (3, 0).

CONCLUSIONS

The purpose of this paper was to show that values of Franck-Condon factors obtained from other works can be calculated with a concise and straightforward way. Using eigenfunctions of Hua potential function, Eq. (4), we calculated the Franck-Condon factors for 10 different band systems of diatomic molecules. It must be emphasized that this work has centered on the accurate solution of Schrödinger equation for Hua potential function and using eigenfunctions of this potential.
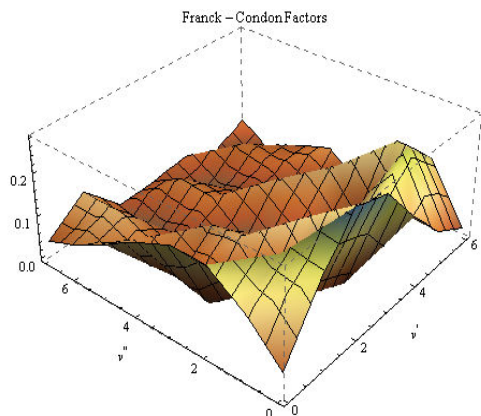
33

Fig. 1: Franck-Condon Factors in 3D for $(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ system of Li_2 .
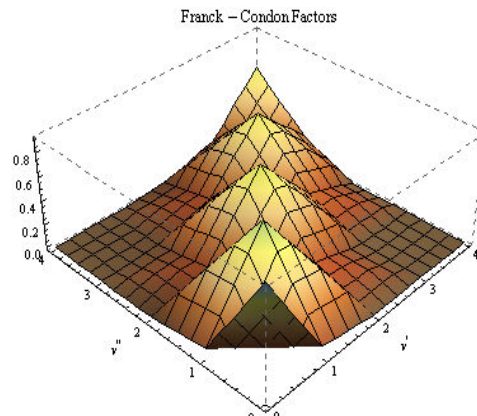

Fig. 3: Franck-Condon Factors in 3D for $(B^2\Sigma^+ - X^2\Sigma^+)$ system of CN.
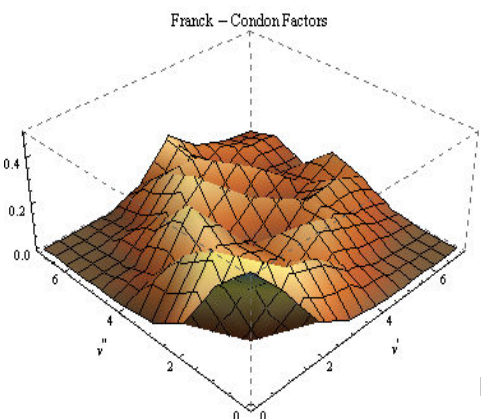

Fig. 2: Franck-Condon Factors in 3D for $(A^2\Pi - X^2\Sigma^+)$ system of CN.
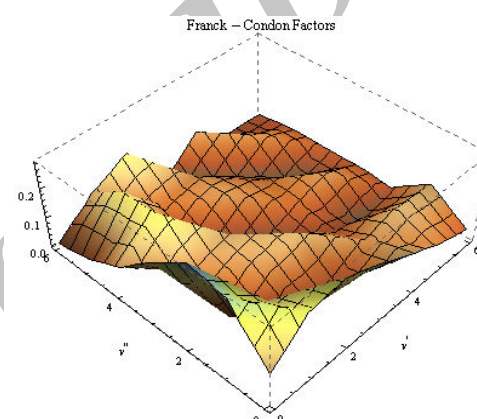

Fig. 4: Franck-Condon Factors in 3D for $(A^1\Pi - X^1\Sigma)$ system of CO.

It is clear from equation (1) that the magnitude of a Franck-Condon factor depends on the degree of overlap between the two vibrational wave functions. This overlap depends on the shapes of the two potentials and their displacements (ΔR_e). It is clearly seen in Figs. 1-4 that the character of the Franck-Condon factor surface $q_{v'v''}$ plotted as a function of v' and v'' depends, in a very sensitive manner, upon the overlap determined by ΔR_e between the two potential involved. When ΔR_e is small (nearly zero), as in the case of $(A^2\Pi - X^2\Sigma^+)$ or $(B^2\Sigma^+ - X^2\Sigma^+)$ systems of CN, the surface is a sharp diagonal ($v' = v''$) ridge which rises to a peak at (0, 0). As ΔR_e increases, the diagonal ridge evolves into one. When ΔR_e is large, as it is for the $(A^1\Pi - X^1\Sigma)$ system of CO, the ridges are separated and surface has many ridges and valleys. Their vertices are remote from (0, 0).

This manner is seen in case of $(B^1\Pi_u - X^1\Sigma_g^+)$ and $(A^1\Sigma_u^+ - X^1\Sigma_g^+)$ systems of Li_2; $(A^3\Sigma_u^+ - X^1\Sigma_g^+)$ and $(a^1\Pi_g - X^1\Sigma_g^+)$ systems of N_2.

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