Calculation of FC F for $Be^9C\ l^{35}$ molecules

Ashwaq Tariq Dahhm Hsoun*

Department of physics, College of science for Women, University of Bagdad, Bagdad, Iraq.

Abstract

Franck-Condon factors (FCF), which are proportional to peak intensities, were calculated as the square of the overlap between the initial and final state wavefunctions in order to calculate of molecule Be^9Cl^{35} their overlap using numerical Integration for the vibrational band ($'v =0 - 4$) to ($v''=0 -4$) of the electronic transition A $^2\prod$ - X $^2 \sum$ and by using an appropriate Potential for each of them .for vibrational ground and first excited states.this new vibrational level must be instantaneously compatible with the nuclear positions and momenta of the vibrational level of the molecule in the originating electronic state. In the semiclassical picture of vibrations (oscillations) of a simple harmonic oscillator, the necessary conditions can occur at the turning points, where the momentum is zero. This leads to, in general, an increase in the "allowed" vibronic transitions and hence greatly influences the observed spectrum. For all but the simplest models for the electronic potentials, one must resort to a numerical calculation of the observed spectrum.

Keywords: Franck-Condon factors, vibronic states, rotational states the ground electronic state, the excited electronic state, Franck–Condon rules

حساب معامل FCF لجزيئة Be9C l35

اشواق طارق دحام*

قسم الفيزياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة:

تحدد معاملات فرانك كوندن احتمالية انتقال الشدة العظمى ، التي يمكن حسابها من مربع التداخل بين الدوال الموجية للحالة الاولية الارضية والحالة النهائية للحالة المتهيجة فلقد تم قياس معاملاتFCF لجزيئة ^{35} Be^{9}Cl باستعمال طريقة التكامل العددي للحزمة الاهتزازية   (4 – 0= v')الى(4 – 0 =v'')   للانتقالات الالكترونية$\sum$ ^{2} X – $\prod^2$ A للحالات الاهتزازية الارضية والمتهيجة باستخدام الاحتمالية المناسبة لكل مرهما. المستويات الاهتزازية الجزيئية الجديدة تتناسب مع المواقع النووية والعزم للمستويات   التوافقية البسيطة للحالة الالكترونية الناشئة . وهذا يكون مشابه للصورة الكلاسيكية للمهتز التوافقي البسيط   . والشرط الضروري الحاصل لنقاط التحول بحيث يكون العزم صفر .وهذا يقود بشكل عام الى ان الانتقالات الاهتزازية سوف تتزايد ويكون تأثيرها كبير على الطيف الملاحظ للنماذج الالكترونية البسيطة المحتملة   ،فلا بد من اللجوء الى الحساب العددي للطيف الملاحظ .

_____
*Email :m _ashwaqtariq@yahoo.com

Introduction

The Franck–Condon principle is a rule in spectroscopy and quantum chemistry that explains the intensity of vibronic transitions. Vibronic transitions are the simultaneous changes in electronic and vibrational energy levels of a molecule due to the absorption or emission of a photon of the appropriate energy. The principle states that during an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significance[1]. The relative intensities of the spectroscopic transitions occurring happens between the ground and excited states could be calculated using electronic transition moment and the overlap happens the vibrational wave functions of the states[2]. Knowing the FCF useful in the investigating of radioactive transitions, atmospheric, chemistry and spectroscopic studies [3] The FCF parameters represent a measure of the overlaps between the wave functions of the ground and excited states, and the square integral value of the overlap was the FCF .The higher parameters values assign to the high intensity of the observe peaks of the vibronic spectrum. The overlap band play role in the complexity of the electronic spectrum ,and for the importance BeCl, Molecule in the chemical and spectroscopic studies, atheortcal and experimental has been carried out , such as Laque and Crossly [4] in determined FCF values , also Langhoff [5], Steffens et al [6], Koperski and Czajknowski [7]and Week et al[8]. During a molecular electronic transition from the ground electronic state to an excited electronic state, the vibreational wave function of the ground state overlap excited state. The degree of overlap between the ground and excited state vibrational function determindes.the shape and structure of the electronic spectrum that is observed [9].In this document we treat the overlap between the ground and excited vibrational states by projecting the ground state vibratinonal wave function onto the excited state. thematically this is equivalent writing the ground state vibrational wave function as a linear combination of the harmonic oscillator wave functions [10]

In this study BeCl, molecule with electronic band A $^2\prod$ - X $^2\sum$ has been investigated ,calculating with high accuracy the FCF values using numerical integration [11].Morse potential especially for vibrational transitions with low vibrational quantum number gives values for potential energy similar to the harmonic model which means the FCF could be calculated for this vibrational quantum numbers while FCF calculation carried out by bates and our calculation for FCF using the integration mentioned in [12] .

Theory

FCF

The intensity of the molecular beam for the vibrational transition $'v \rightarrow v''$ within any electronic transition is given bends y the following relation[13]:

I = D$N_{v'}$ E4 Re(r $_{v'v''}$)q $_{v'v''}$ (1)

Where D is constant depends on the geometry of the apparatus used in the laboratory ,N$_{v'}$ is the relative population for the v', E$_{v'v''}$ is the quantum energy for the transition , q$_{v'v''}$ is the FCF ,r$_{v'v''}$ is the r – centroid ,and Re is the electronic transition moment . The square of the the integral of the overlap i.e. FCF given by the following relation[14] :

q$_{v'v''}$=$|\langle\Psi_{v'}|\Psi_{v''}\rangle|^2$ (2a)

Or

q$_{v'v''}$=$|\int\Psi_{v'v''}\ \Psi_{v'v''}dr|^2$ (2b)

Where $\Psi_{v'}$, $\Psi_{v''}$ are the two wave vabrational functions for the upper and lower states respectively.

$$\int \psi_e'^* \boldsymbol{\mu}_e \psi_e d\tau_e \int \int \psi_v'^* \psi_e'^* \boldsymbol{\mu}_e \psi_e \psi_v d\tau_e d\tau_n \approx \int \psi_v'^* \psi_v d\tau_n \int \psi_e'^* \boldsymbol{\mu}_e \psi_e d\tau_e.$$ (3)

This factorization would be exact if the integral over the spatial coordinates of the electrons would not depend on the nuclear coordinates. However, in the Born-Oppenheimer approximation ψ_e and ψ_e' do depend (parametrically) on the nuclear coordinates, so that the integral (a so-called transition dipole surface) is a function of nuclear coordinates. Since the dependence is usually rather smooth its neglect (i.e., the assumption that the transition dipole surface is independent of nuclear coordinates, called the Condon approximation) is often allowed.The first integral after the plus sign is equal to zero

because electronic wavefunctions of different states are orthogonal. Remaining is the product of three integrals. The first integral is the vibrational overlap integral, also called the Franck-Condon factor. The remaining two integrals contributing to the probability amplitude determine the electronic spatial and spin selection rules.In our study, we utilized the Harmonic Oscillator wave functions as an approximation formodeling molecular vibrations. Harmonic Oscillator wave functions (Ψv) are of the form:

$$\Psi v(x) = N v H v (\alpha^{\frac{1}{2}} x) e^{-\alpha x^2 \backslash 2} \qquad (4)$$

where $N v$ is a normalization constant

$$N v = \frac{1}{(2^v v!)^{\frac{1}{2}}} \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \qquad (5)$$

α depends on the molecular characteristics of the bond,

$$\alpha = \left(\frac{K\mu}{\hbar^2}\right)^{\frac{1}{2}} \qquad (6)$$

K represents the force constant of the bond, and μ represents the reduced mass. The Franck Condon Principle considers the overlap of excited and ground state wave functions in determining transition probability. Franck-Condon factors were calculated using equation 2b. [15].The Franck–Condon principle is a statement on allowed vibrational transitions between two *different* electronic states, other quantum mechanical selection rules may lower the probability of a transition or prohibit it altogether. Rotational selection rules have been neglected in the above derivation. Rotational contributions can be observed in the spectra of gases but are strongly suppressed in liquids and solids.It should be clear that the quantum mechanical formulation of the Franck–Condon principle is the result of a series of approximations, principally the electrical dipole transition assumption and the Born-Oppenheimer approximation. Weaker magnetic dipole and electric quadruple electronic transitions along with the incomplete validity of the factorization of the total wave function into nuclear, electronic spatial and spin wave functions means that the selection rules, including the Franck-Condon factor, are not strictly observed [16].the electronic transition, the molecules which end up in higher vibrational states immediately begin to relax to the lowest vibrational state. In the case of solvation, the solvent molecules will immediately try to rearrange themselves in order to minimize the interaction energy. The rate of solvent relaxation depends on the viscosity of the solvent. Assuming the solvent relaxation time is short compared with the lifetime of the electronic excited state, emission will be from the lowest solvent energy state of the excited ectronic state. the Franck–Condon principle applied to solvation. When the solution is illuminated by with light corresponding to the electronic transition energy, some of the chromospheres will move to the excited state. Within this group of chromospheres there will be a statistical distribution of solvent-chromospheres interaction energies, the solvent-chromospheres traction is drawn as a parabolic potential in both electronic states [17]. The electronic transition is essentially instantaneous on the time scale of solvent motion (vertical arrow), the collection of excited state chromospheres is immediately far from equilibrium. The rearrangement of the solvent molecules according to the new otential energy curve is represented by the curved arrows. Note that while the electronic transitions are quantized, the chromospheres-solvent interaction energy is treated as an ssical continuum due to the large number of molecules involved. Although emission is depicted as taking place from the minimum of the excited state chromospheres-solvent interaction potential, significant emission can take place before equilibrium is reached when the viscosity of the solvent is high or the lifetime of the excited state is short[18].

Theoretical result

In the present work, the spectroscopic constants are list in table. 1

Morse potential function for ground and excited states has been carried out from the experimental data by Haber and Herzberg [19] and the integral mentioned in equation (2) has been numerically calculated using Dirac- delta function for the bands v=0,1,2,3,4 and $\acute{v}$=0,1,2,3,4 as shown in Table(1) and table-2:

The Franck-Condon principle states that after a molecule are excited from its ground electronic state the nuclear conformation must readjust. This leads to, in general, an increase in the "allowed" vibronic transitions and hence greatly influences the observed spectrum. For all but the simplest models for the

electronic potentials, one must resort to a numerical calculation of the observed spectrum. However if we are able to determine the functional form for the wave functions of more complicated models, we can utilize the analytic capabilities of *Mathematical* to calculate the (Franck-Condon) spectrum. There are a number of interesting models which are simple enough to determine the wave functions yet to complicated to work out the theoretical spectra by hand. This project also has application to the vibrational spectra of molecules in the condensed phase.

Table 1 - spectral constants (cm^{-1}) used as input data for calculation for Be^{9}Cl^{35} Molecule [20]

Spectroscopic Constant	$X^2\Sigma^+$ (cm^{-1})	$A^2\prod$ (cm^{-1})
Te	0	27970.5
ω_e	846.58	824.19
ω_{exe}	5.11	6.03

Table 2- FCF A-X system of Be^{9}Cl^{35} (v'=0—4), (v''=0—4).

v'\v''	0	1	2	3	4
0	0.999910202	0.362875619	0.121661271	0.015119817	3.02331E-09
1	0.628050549	0.56234848	0.183007994	7.48358E-06	0.005841839
2	0.271264677	0.176607495	0.623162203	0.088462906	0.201953991
3	0.235518956	0.05272017	0.107632857	0.249708285	0.096295602
4	0.306117486	0.458415399	0.115480754	0.082714331	2.10048E-09

Conclusions

The values of FCF for A-X electronic transition shows that for the vibrational bands Δv =0 has higher intensity of Be^{9}Cl^{35} molecule followed by less intensity of $\Delta v=\pm1$ This is in consisten with the expected quantum theoretical values for Franck –Condon principle. In the Franck-Condon principle two different electronic states ψ'_e and ψ_e, with corresponding (large) electronic excitation energy. The F-C principle accounts for vibrational structure on top of this electronic transition. It is assumed that both factors (electronic dipole and vibrational overlap) of integral are non-zero. Different magnitudes of the vibrational overlap integral give different intensities of the vibrational lines superimposed on one and the same electronic transition.

References
1. Wright, J.C.; Zielinski, T. J,. **1999.** "Franck-Condon Factors and Their Use in undergraduateQuantum Mechanics", *J. Chem. Ed.*, 76, pp:1367-1373.
2. Prithivi K. N. and Rajamamickam N., **.2002.** Rev. Mex. vol.48,5, 432.
3. Liboff, Richard L**. 2002**. *Introductory Quantum Mechanics*. Addison-Wesley.
4. Oel M. Bowman , Xinchuan Huang , Lawrence B. Harding , Stuart Carter . **2006. "**The determination of molecular properties from MULTIMODE with an application to the calculation of Franck–Condon factors for photoionization of CF3to*" Molecular Physics*; 104, pp: 33.
5. Manfred Lein . **2007.** Molecular imaging using recolliding electrons. *Journal of Physics B: Atomic, Molecular and Optical Physics*; 40: R135.
6. Grimpe A, Figl C, Grosser J, Hoffmann O, Rebentrost F**. 2005.** Oscillatory differential cross sections for Li + He, Ne, H2 and D2 optical collisions. *Journal of Physics B: Atomic, Molecular and Optical Physics;* 38, pp*: 135.*
7. Karthikeyan, **. 2007 .**, Studies on Molecular Species Identified in Solar and Allied Spectra by Spectroscopic Techniques, PhD thesis, University of Madurai, India, December.
8. Weck P.F., Kirby K. and Stancll P.C.**.2004**. *,J.Chem. phys,* Vol. 120, No.9.,pp:4216- 4222,
9. Benjamin Lasorne , Graham A. Worth , Michael A. Robb . **2011.** Excited-state dynamics. Wiley Interdisciplinary Reviews: *Computational Molecular Science*; 1, pp,: 460.

10. Joel M Bowman , Tucker Carrington , Hans-Dieter Meyer **. 2008.** ariational quantum approaches for computing vibrational energies of polyatomic molecules. *Molecular Physics*; 106: 2145

11. Salam A., Micha D.A.**.2010 .** Photoinduced quantum dynamics in molecules and at adsorbate.s. *Molecular Physics*; 108, pp: 3223

12. Angela Acocella , Garth A. Jones , Francesco Zerbetto**. 2012 .** Excitation Energy Transfer and Low-Efficiency Photolytic Splitting of Water Ice by Vacuum UV Light. *The Journal of Physical Chemistry Letters*; **3**: 3610.

13. Vibók Á., Csehi A., Gindensperger E., Köppel H., Halász G. J**.. 2012.** Quantum Dynamics through Conical Intersections: Combining Effective Modes and Quadratic Couplings. *The Journal of Physical Chemistry A*; 116, pp: 2629.

14. Julian Albert , Alexander Schubert , Volker Engel **. 2013.** Two-dimensional vibronic spectroscopy of molecular predissociation. *New Journal of Physics*; 15, pp: 025008.

15. Lina Cheng , Kaijun Yuan , Yuan Cheng , Qing Guo , Xueming Yang , Richard N. Dixon **. 2010.** Product rotational Franck–Condon oscillations in HOD (Jka,kc) dissociation. *Molecular Physics*; 108, pp: 905

16. Panayiotis C. Varras , Antonios K. Zarkadis **. 2012.** Ground- and Triplet Excited-State Properties Correlation: A Computational CASSCF/CASPT2 Approach Based on the Photodissociation of Allylsilanes. *The Journal of Physical Chemistry A*; 116, pp:1425.

17. Binney James and Skinner, D**. 2010.** *The Physics of Quantum Mechanics: An Introduction* (3rd ed.).

18. Shanmugavel, R**. 2007.** Investigations on the Molecular Band Spectra of Astronomical and Chemical Environment, PhD thesis, University of Madurai, India, December.

19. Ying-Chih Chiang , Frank Otto , Hans-Dieter Meyer , Lorenz S. Cederbaum**. 2011.** Interrelation between the Distributions of Kinetic Energy Release and Emitted Electron Energy following the Decay of Electronic States. *Physical Review Letters*; 107.

20. Huber, K.P. and Herzberg, G., **.2005.** "Constants of Diatomic Molecules" (data prepared by J.W.Gallagher and R.D. Johnson, III) in NIST Chemistry WebBook, NIST Standard Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, June, National Institute of Standards and Technology, Gaithersburg MD, 20899 .