SIMPLE DERIVATION OF FRANCK-CONDON INTEGRALS

S. Gharanfoli and R. Islampour*

Department of Chemistry, Teacher Training University, Tehran, Islamic Republic of Iran

Abstract

The expressions for vibrational overlap integrals of the one-dimensional harmonic wavefunctions (centered about different equilibrium positions and having different frequencies) have been derived in a simple and straightforward way.

Introduction

In general, the vibrational structure of an electronic ectrum is determined by two quantities: the dependence the electronic transition moment upon the nuclear co-dinates and the change in molecular dimensions upon ectronic excitation. Given the change in the molecular mensions, and the force fields for the two linking elec-onic states, the Franck-Condon principle allows the in-nsity distribution to be calculated.

Within the Born-Oppenheimer approximation [1], the ansition dipole moment (which determines the intensity f an optical transition) for a vibronic transition between e v"th vibrational level in the lower electronic state a and e v'th vibrational level of the upper state b is given by[‡]

$$\langle av''|\hat{M}|bv'\rangle = \int \chi^*_{v''}(Q'')\left[\int \Phi^*_a(r,Q'')\hat{M}(r)\Phi_b(r,Q')\,d^3r\right]\chi_{v'}(Q'')\,dQ'', \quad (1)$$

where r and Q denote the sets of electronic and vibrational ariables; $\Phi(r,Q)$ and $\chi(Q)$ represent electronic and vibra-ional wave functions respectively, and $\hat{M}(r)$ is the electric lipole operator. It is customary to assume that the elec-ronic transition moment

$$\mu_{ab}(Q) = \int \Phi^*_a(r,Q'')\hat{M}(r)\Phi_b(r,Q')\,d^3r \quad (2)$$

is a slowly varying function of the vibrational variables, and to expand the transition moment about the equilibrium configuration of one of the two electronic states as power series in the vibrational variables Q' or Q"

$$\mu_{ab}(Q) = \mu_{ab}(o) + (d\mu_{ab}/dQ'').\,Q''+\ldots$$
$$= \mu_{ab}(o) + (d\mu_{ab}/dQ').\,Q'+\ldots \quad (3)$$

If we retain only the first (constant) term in these expansions: $\mu_{ab}(Q) \simeq \mu_{ab}(o)$, the transition dipole moment is then given by

$$\langle av''|\hat{M}|bv'\rangle \simeq \mu_{ab}(o)\langle v''|v'\rangle \quad (4)$$

The approximation embodied in this equation is known in electronic spectroscopy as the Condon approximation [2]. This leads to the usual Franck-Condon [3] description of the intensity distribution within a band in terms of square of vibrational overlap integral $|\langle v''|v'\rangle|^2$.

The expression for vibrational overlap integrals of the one-dimensional harmonic wavefunctions (centered about different equilibrium positions and having different frequencies) was first evaluated in 1930 by Hutchisson [4], who used finite-series expansions. Manneback [5], Wagner [6], and Ansbacher [7] in 1959 derived various formulas of which Ansbacher's are mostly used (see also [8] and [9]). The work of Koide [10] obtains the general formula for

Keywords: Franck-Condon integrals; Radiative and non-adiative processes

‡We adopt the common spectroscopic notations, whereby we label lower state quantities by a double prime and upper state quantities by a single prime.

FC factors, not explicitly, but in terms of a differential operator. On the other hand, Katriel [11] gives it as a triple summation. Palma and Morales [12] reconsidered these derivations using the second quantization formalism.

It is the purpose of this paper to show that all Ansbacher's formulas can be obtained completely with a simple and straightforward derivation.

Closed Formulas for the Overlap Integral

Let us consider two displaced one-dimensional harmonic oscillators with different frequencies ω", ω' and respective Hamiltonians

$$\hat{H}_a=\frac{1}{2}(\hat{P}''^2+\omega''^2Q''^2),\quad \hat{H}_b=\frac{1}{2}(\hat{P}'^2+\omega'^2Q'^2),\quad (5)$$

where $\hat{P}$ is the conjugate momentum to the mass-weighted vibrational coordinate Q. These two oscillators are centered at different equilibrium positions and have different force constants. The positions for both oscillators are related to each other by

$$Q' = Q'' + d. \quad (6)$$

The vibrational wave function is given by

$$\chi_v(Q) = (\alpha/\pi^{1/2}\, 2^v\, v!)^{1/2}\, H_v(\alpha Q)\exp(-\alpha^2Q^2/2), \quad (7)$$

where $\alpha = (\omega/h)^{1/2}$ and $H_v(\alpha Q)$ are Hermite polynomials.

We wish to evaluate the integral

$$\langle v''|v'\rangle=\int_{-\infty}^{+\infty}\chi_{v''}(Q'')\chi_{v'}(Q')\,dQ''$$

$$=(\alpha''/\pi^{1/2}2^{v''}v''!)^{1/2}(\alpha'/\pi^{1/2}2^{v'}v'!)^{1/2}\times \quad (8)$$

$$\int_{-\infty}^{+\infty}H_{v''}(\alpha''Q'')H_{v'}(\alpha'Q')\exp(-\alpha''^2Q''^2/2-\alpha'^2Q'^2/2)dQ''$$

Substituting equation (6) in equation (8) and making a transformation to a new variable $x=[(\alpha'^2+\alpha''^2)/2]^{1/2}[Q''+\alpha'^2d/(\alpha'^2+\alpha''^2)]$, we may then write equation (8) as

$$\langle v''|v'\rangle=\pi^{-1/2}N_{v''v'}\,I_{v''v'} \quad (9)$$

where

$$I_{v''v'}=\int_{-\infty}^{+\infty}H_{v''}(\alpha_2x+\delta_2)H_{v'}(\alpha_1x+\delta_1)\exp(-x^2)dx, \quad (10)$$

$$N_{v''v'}=(2^{v''+v'}v''!v'!)^{-1/2}[2\beta/(1+\beta^2)]^{1/2}\exp[-\alpha''^2\beta^2d^2/2(1+\beta^2)], \quad (11)$$

$$\alpha_1=\sqrt{2}\beta/(1+\beta^2)^{1/2},\quad \delta_1=\beta\alpha''d/(1+\beta^2), \quad (12)$$

$$\alpha_2=\sqrt{2}/(1+\beta^2)^{1/2},\quad \delta_2=-\beta^2\alpha''d/(1+\beta^2), \quad (13)$$

and $\beta=\alpha'/\alpha''$.

The integral in equation (10) can be evaluated by using the generating functions for the Hermite polynomials

$$\sum_{v'}\frac{H_{v'}(z_1)}{v'!}s_1^{v'}=\exp(-s_1^2+2s_1z_1) \quad (14)$$

$$\sum_{v''}\frac{H_{v''}(z_2)}{v''!}s_2^{v''}=\exp(-s_2^2+2s_2z_2) \quad (15)$$

If these expressions are multiplied together and also multiplied by the exponential in equation (10), and use is made of the Gaussian integration formula

$$\int_{-\infty}^{+\infty}\exp[-(ax^2+bx+c)]\,dx=(\pi/a)^{1/2}\exp[(b^2-4ac)/4a], \quad (16)$$

we obtain

$$\sum_{v'v''}\frac{\langle v''|v'\rangle}{N_{v''v'}(v''!v'!)}s_1^{v'}s_2^{v''}=\exp[-As_1^2+2Bs_1s_2+As_2^2+2s_1\delta_1+2s_2\delta_2] \quad (17)$$

where

$$A=(1-\beta^2)/(1+\beta^2)\qquad B=2\beta/(1+\beta^2) \quad (18)$$

Expanding the exponential function on the right hand side of equation (17) and then equating the like powers of s_1 and s_2 on both sides of the equation, we obtain the following general expression

$$\langle v''|v'\rangle=N_{v''v'}(v''!\,v'!)\sum_l\frac{(2B)^l}{l!}\sum_k\frac{(-1)^kA^k(2\delta_1)^{v'-2k-l}}{k!(v'-2k-l)!}\sum_m\frac{A^m(2\delta_2)^{v''-2m-l}}{m!(v''-2m-l)!} \quad (19)$$

$$N_{v'v'}(v''!v'!)A^{(v'+v'')/2}\sum_{l}(2B/A)^{l}\frac{1}{l!}(-i)^{v''-l}$$

$$\frac{(-1)^{k}(2A^{-1/2}\delta_1)^{v'-2k-l}}{k!(v'-2k-l)!}\times\sum_{m}\frac{(-1)^{m}(2iA^{-1/2}\delta_2)^{v''-2m-l}}{m!(v''-2m-l)!} \quad (20)$$

ıere k goes over 0 to (v'-l)/2 or (v'-l-1)/2, and m over 0 (v"-l)/2 or (v"-l-1)/2.

By making use of the definition of the Hermite polyno- ıals

$$H_n(x)=\sum_{k=0}(-1)^{k}\frac{n!}{k!(n-2k)!}(2x)^{n-2k}, \quad (21)$$

ɜ can write equation (20) as

$$\langle v''|v'\rangle=N_{v''v'}\sum_{l=0}^{(v',v'')}l!(2B)^{l}\binom{v'}{l}\binom{v''}{l}(-i)^{v''-l}A^{(v'+v''-2l)/2}\times$$

$$H_{v'-l}(A^{-1/2}\delta_1)H_{v''-l}(iA^{-1/2}\delta_2) \quad (22)$$

here (v', v") means the smaller of v' and v"; and $\binom{k}{l}$ presents the binomial coefficient. Equation (22) which is uivalent to Ansbacher's formula (7) is the general ex- ession for the vibrational overlap integral of a displaced- storted system. In particular,

$$\langle 0|v'\rangle=N_{0v'}A^{v'/2}H_{v'}(A^{-\frac{1}{2}}\delta_1) \quad (23a)$$

$$\langle v''|0\rangle=N_{v''0}(-i)^{v''}A^{v''/2}H_{v''}(iA^{-\frac{1}{2}}\delta_2) \quad (23b)$$

ɔ derive the well-known recurrence relations given by nsbacher, we may make use of equation (17). Taking rivatives of this equation with respect to s_1 and s_2 and ıuating the like powers of s_1 and s_2 on both sides of the sulting equation, we easily obtain

$$\langle v''|v'\rangle=\delta_2(2/v'')^{\frac{1}{2}}\langle v''-1|v'\rangle+B(v'/v'')^{\frac{1}{2}}\langle v''-1|v'-1\rangle$$
$$+A\{(v''-1)/v''\}^{\frac{1}{2}}\times\langle v''-2|v'\rangle \quad (24a)$$

$$\langle v''|v'\rangle=\delta_1(2/v')^{\frac{1}{2}}\langle v''|v'-1\rangle+B(v''/v')^{\frac{1}{2}}\langle v''-1|v'-1\rangle$$
$$-A\{(v'-1)/v'\}^{\frac{1}{2}}\times\langle v''|v'-2\rangle \quad (24b)$$

Some Limiting Cases

(i) Displaced Oscillator

For two harmonic oscillators having the same frequency β=1, B= 1, A= 0, and noticing that $\lim_{\alpha\to 0}\alpha^{n/2}H_n(x\alpha^{-1/2})=(2x)^n$, equation (22) reduces to

$$\langle v''|v'\rangle=N_{v''v'}\sum_{l=0}^{(v',v'')}l!\binom{v'}{l}\binom{v''}{l}(2\delta_1)^{v'-l}(2\delta_2)^{v''-l} \quad (25)$$

where for this case $\delta_1=-\delta_2=\alpha''\delta/2$. This expression can be written in terms of the associated Laguerre polynomials

$$L_n^k(x)=\sum_{m=0}^{\infty}\frac{(-1)^m(n+k)!}{(n-m)!(k+m)!m!}x^m \quad (26)$$

The result is

$$\langle v''|v'\rangle=\exp(-\alpha''^2d^2/4)(v''!/v'!)^{1/2}(\alpha''d/\sqrt{2})^{v'-v''}L_{v''}^{v'-v''}(\alpha''^2d^2/2),\ v>v'' \quad (27a)$$

$$\langle v''|v'\rangle=\exp(-\alpha''^2d^2/4)(v'!/v''!)^{1/2}(-\alpha''d/\sqrt{2})^{v''-v'}L_{v'}^{v''-v'}(\alpha''^2d^2/2),\ v''>v' \quad (27b)$$

Therefore,

$$\langle 0|v'\rangle=\frac{1}{\sqrt{v'!}}(\alpha''d/\sqrt{2})^{v'}\exp(-\alpha''^2d^2/4) \quad (28a)$$

$$\langle v''|0\rangle=\frac{1}{\sqrt{v''!}}(-\alpha''d/\sqrt{2})^{v''}\exp(-\alpha''^2d^2/4) \quad (28b)$$

(ii) Distorted Oscillator

For the case in which the displacement between the two oscillators is zero, $\delta_1=\delta_2=0$, and equation (22) becomes

$$\langle v''|v'\rangle=B^{1/2}(A/2)^{(v'+v'')/2}(v'!v''!)^{1/2}\sum_{l}(2B/A)^{l}\frac{(-i)^{v''-l}}{l!(v'-l)!(v''-l)!}\times$$
$$H_{v'-l}(0)H_{v''-l}(0) \quad (29)$$

Noticing that $H_{2n}(0)=(-1)^n2^n(2n-1)!!=(-1)^n(2n)!/n!$, $H_{2n+1}(0)=0$, we may write equation (29) as

$$\langle v'+2q|v'\rangle=B^{1/2}(A/2)^{v'+q}\{(v'+2q)!v'!\}^{1/2}\sum_{l}(2B/A)^{v'-2l}$$
$$\frac{(-1)^{l}}{(v'-2l)!l!(l+q)!} \quad (30a)$$

$$\langle v''|v''+2q\rangle = B^{1/2}(A/2)^{v''+q}\{(v''+2q)!v''!\}^{1/2}\sum_{l}(2B/A)^{v''-2l}\frac{(-1)^{l+q}}{(v''-2l)!\,l!\,(l+q)!} \quad (30b)$$

In particular,

$$\langle 0|2q\rangle = \frac{\{(2q)!\}^{1/2}}{q!}(-1)^{q}B^{1/2}(A/2)^{q}, \quad (31a)$$

$$\langle 2q|0\rangle = \frac{\{(2q)!\}^{1/2}}{q!}B^{1/2}(A/2)^{q} \quad (31b)$$

In summary, we have presented a general formulation for the one-dimensional overlap integrals in a simple and easy-to-follow method, in contrast with the previous derivations which involve differential operators [10], a triple summation expression [11], or second quantization formalism [12].

Franck-Condon factors are widely used in formulating the radiative [13, 14] and the non-radiative (e.g. electron transfer [15] and electronic relaxation [16] processes.

References

1. Born, M. and Oppenheimer, J.R. *Ann. Physik*, **84**, 457, (1927).
2. Condon, E.U. *Phys. Rev.*, **32**, 858, (1928).
3. Franck, J. *Trans. Faraday Soc.*, **21**, 536, (1925).
4. Hutchisson, E. *Phys. Rev.*, **36**, 410, (1930).
5. Manneback, C. *Physica.*, **17**, 1001, (1951).
6. Wagner, M. *Z. Naturforsch. Teil*, **A14**, 81, (1959).
7. Ansbacher, F. *Ibid.*, 889, (1959).
8. Terasaka, T. and Matsushita, M. *Chem. Phys. Lett.*, **80**, 306, (1981).
9. Waldenstrom, S. and Naqvi, K.R. *Ibid.*, **85**, 581 (1982).
10. Koide, S. *Z. Naturforsch. Teil*, **A15**, 123, (1960).
11. Katriel, J. *J. Phys.*, B **3**, 1315, (1970).
12. Palma, A. and Morales, J. *Int. J. Quantum Chem.*, **17**, 393, (1983).
13. Islampour, *R. Chem. Phys.*, **133**, 425, (1989); Islampour, R. and Lin, S.H. *Trends in Chem. Phys.*, **1**, 249, (1991).
14. Islampour, R., Hayashi, M. and Lin, S.H. *J. Chem. Phys.* (Submitted).
15. Islampour, R. and Lin, S.H. *Chem. Phys. Lett.*, **179**, 147, (1991); *J. Chem. Phys.*, **95**, 10261, (1991); *J. Phys. Chem.*, **97**, 6793, (1993).
16. Islampour, R. and Gharanfoli, S. *Chem. Phys.* (In press).