FRANCK-CONDON FACTORS FOR DIATOMIC MOLECULES

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We have investigated the validity of the harmonic-oscillator approximation for the calculation of the Franck–Condon factors (FCF) of diatomic molecules. Our results show that, although in general the FCF obtained with this approximation exhibit the correct order of magnitude, they fail to predict the relative magnitudes of off-diagonal elements of the FCF-array obtained by more accurate methods. We show that this deficiency of the harmonic-oscillator approximation is overcome if the cubic term in the expansion of the potential-energy function about equilibrium is taken properly into account. Second-order perturbation theory, i.e. incorporating the cubic and quartic terms of the Dunham expansion, corrects this transposition of the FCF array caused by the harmonic-oscillator approximation. We also show that the FCF array obtained through the harmonic approximation is almost the transpose of the array obtained by more accurate means. For this reason the relative FCF calculated by means of the harmonic approximation agree remarkably well with the relative intensities obtained from electron impact experiments.

1. Introduction

Franck–Condon factors (FCF) are of the utmost importance in the study of vibronic transitions [1]. Within the Born–Oppenheimer approximation, the intensities of the absorption or emission bands are proportional to the FCF [1]. For this reason several methods have been proposed to calculate them. According to current practice, the most accurate FCF are based on the Rydberg–Klein–Rees (RKR) potential energy [2]. As RKR potentials consist of pairs of classical turning points, one has to resort to appropriate algorithms for numerical integration in order to obtain the wavefunctions [3] of which the FCF are the squares of the overlap integrals.

An alternative way to calculate FCF is based on model potentials for which the Schrödinger equation may be exactly solved. Of such simple models the most realistic is the Morse function [4]. However, although the Schrödinger equation thereof is exactly soluble, the FCF are obtained in closed form only under certain simplifying assumptions [5]. Furthermore, as the expressions for the overlap integrals appear complicated, it seems preferable to carry out the integration numerically.

The Kratzer function [6] has been recently proposed for the calculation of FCF [7]. Not only is this potential less realistic than that due to Morse but also it leads to overlap integrals that can be solved only approximately [7].

The only exactly soluble model for which one obtains the overlap integrals in closed form is the canonical harmonic oscillator. Many methods to calculate two-centre integrals and matrix elements between harmonic-oscillator eigenfunctions have been proposed, some of them being equivalent [8]. Because of the simplicity of the boson algebra, one can readily derive generating functions and recurrence relations in closed form for various two-centre integrals and matrix elements [9]. The use of non-normalized coherent states facilitates the calculation [10]. In our opinion, recurrence relations [9–11] are the most practicable for computational purposes if one is interested either in numerical calculation or in analytic expressions produced by means of computer algebra. Generating functions are commonly suitable to derive useful analytic expressions involving sums of integrals [12].

Although the harmonic approximation is less realistic than the Morse function, its simplicity, which

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enables one to calculate both analytic approximate FCF for polyatomic molecules and matrix elements between harmonic-oscillator wavefunctions in many dimensions [12,13], makes it attractive. The simplest harmonic-oscillator approach to diatomic molecules consists of using an average frequency for both electronic states involved in the transition [14]. That the FCF depend on only one parameter facilitates a comparative analysis of their behaviour [15]. The disadvantage of this simplification is that the array of FCF obtained in this way is symmetric whereas the actual array is non-symmetric. This symmetry disappears when the distinct values of the vibrational frequencies of both states are taken into account [16].

As our interest lies in accurate analytic expressions for FCF we investigate here whether the harmonic approximation is a reliable tool for the interpretation of molecular vibronic spectra. We restrict ourselves firstly to diatomic molecules for which there are many data and secondly to low vibrational states for which the harmonic oscillator may lead to a useful approximation. We compare the FCF calculated for the harmonic oscillator with those from more realistic approximations in section 2 and with experimental data in section 3. We discuss the scope and limitations of the harmonic approximation in section 4.

2. Franck–Condon factors for the Dunham potential-energy function

According to the Born–Oppenheimer approximation and the assumption that the electronic transition moment varies slowly with internuclear separation R, the intensity of a vibronic band in absorption or emission is proportional to the FCF [1],

$$q(v',v'')=|S_{v''v'}|^2\,, \tag{1}$$

where $S_{v''v'}$ is the overlap integral between the vibrational states v'' and v' for which the wavefunctions are $\psi''_{v''}$ and $\psi'_{v'}$, respectively. Thus,

$$S_{v''v'}=\int \psi''_{v''}\psi'_{v'}\,\mathrm{d}R\,, \tag{2}$$

according to conventional notation to denote electronic states of lesser ($''$) and greater ($'$) energy. As stated above, one can use several approaches to estimate the FCF. The Dunham expansion [17] is most suitable for our present purpose as shown below.

For small enough displacements from the equilibrium distance R_e, the interatomic potential $V(R)$ for a diatomic molecule can be expanded in a power series of $x=(R-R_e)/R_e$ [17]:

$$V(R)=a_0x^2(1+a_1x+a_2x^2+...)\,. \tag{3}$$

The coefficients a_j are determined from the vibration–rotational spectrum of the molecule. We neglect terms of order larger than those shown in eq. (3) because they are unnecessary for the present discussion. The coefficients a_0, a_1, and a_2 are related to the standard spectroscopic parameters as follows:

$$a_0=\omega_e/4B_e\,,$$
$$a_1=-1-\alpha_e\omega_e/(6B_e)^2\,,$$
$$a_2=5a_1^2/4-2\omega_ex_e/3B_e\,. \tag{4}$$

The expansion (3) leads to reasonably accurate FCF for small vibrational quantum numbers (typically, $v\leqslant 4$) provided that the terms of larger order are not too great. We calculate the FCF by means of an iterative procedure described in detail elsewhere [18]. To this end we expand the vibrational wavefunction ψ_v of each electronic state as a linear combination of the eigenfunctions ϕ_j of the harmonic-oscillator Hamiltonian operator

$$H_0=p^2/2\mu+a_0x^2\,,\quad p=-\mathrm{i}\hbar\,\mathrm{d}/\mathrm{d}x\,. \tag{5}$$

It is convenient to write ψ_v for each electronic state as

$$\psi_v=\sum_{j=v-N}^{v+N} c_{jv}\phi_j\,, \tag{6}$$

in which it is assumed that $c_{jv}=0$ if $j<0$. In this way, when $N=0$ we have the harmonic-oscillator approximation because the Ansatz (6) is reduced to one term. If the vibrational wavefunction of each electronic state calculated in this way is normalized to unity then the overlap integrals become

$$S_{v''v'}=\sum_{j=v''-N}^{v''+N}\sum_{k=v'-N}^{v'+N} c''_{jv''}c'_{kv'}\int \phi''_j\phi'_k\,\mathrm{d}R\,. \tag{7}$$

These harmonic-oscillator two-center overlap integrals are readily obtained recursively [9–11].

Using standard spectral data [19], we have calculated the FCF for the following transitions:

$\mathrm{CN}\ (\mathrm{X}\ {}^1\Sigma^+) \leftarrow \mathrm{CN}\ (\mathrm{A}\ {}^2\Pi_i, \mathrm{B}\ {}^2\Sigma^+)$,

$\mathrm{CO}\ (\mathrm{X}\ {}^1\Sigma^+) \leftarrow \mathrm{CO}\ (\mathrm{a}\ {}^3\Pi_r, \mathrm{a}'\ {}^3\Sigma^+, \mathrm{A}\ {}^1\Pi, \mathrm{b}\ {}^3\Sigma^+)$,

$\mathrm{H_2}\ (\mathrm{X}\ {}^1\Sigma_g^+) \leftarrow \mathrm{H_2}\ (\mathrm{B}\ {}^1\Sigma_u^+)$,

$\mathrm{HCl}\ (\mathrm{X}\ {}^1\Sigma^+) \leftarrow \mathrm{HCl}\ (\mathrm{V}\ {}^1\Sigma^+)$,

$\mathrm{N_2}\ (\mathrm{X}\ {}^1\Sigma_g^+) \leftarrow \mathrm{N_2}\ (\mathrm{A}\ {}^3\Sigma_u^+, \mathrm{B}\ {}^3\Pi_g, \mathrm{a}\ {}^1\Pi_g, \mathrm{C}\ {}^3\Pi_u)$,

$\mathrm{O_2}\ (\mathrm{X}\ {}^3\Sigma_g^-) \leftarrow \mathrm{O_2}\ (\mathrm{A}\ {}^3\Sigma_u^+)$.

In each case we have calculated the FCF with increasing size of the basis sets until convergence was attained. The results show a striking behaviour, an example of which is shown in fig. 1 for the CN "red bands"; i.e. the system $\mathrm{X}\ {}^2\Sigma^+ \leftarrow \mathrm{A}\ {}^2\Pi$. It is clear that the harmonic-oscillator approximation ($N=0$) predicts the relative values of $q(k, j)$ and $q(j, k)$, $j \neq k$, in the reversed order even for the smallest vibrational quantum numbers. We found this behaviour to apply to all cases studied. In order to be certain that it is not an artifact of our numerical method, we have checked the converged results by means of an independent calculation based on the numerical integration of the vibrational eigenfunctions for the Morse potential energy. Moreover, the FCF calculated for the Dunham oscillator agree with the most accurate ones reported in the literature. We thus conclude that the transposition caused by the harmonic-oscillator approximation is mainly due to the neglect of the cubic and quartic terms in the expansion of the potential-energy function around equilibrium.

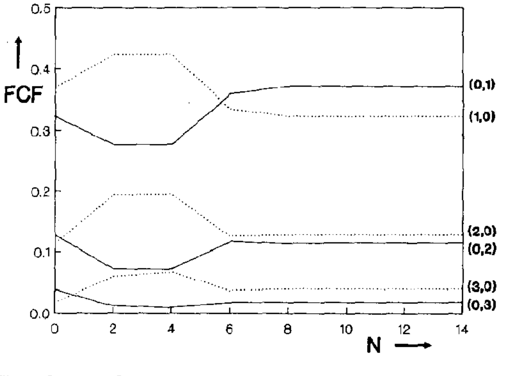

Fig. 1. Values of the Franck–Condon factors FCF for the CN red bands (v', v'') calculated by means of the basis-set expansion indicated in eqs. (6) and (7) as a function of the number N of basis functions.

We tried to improve the harmonic-oscillator approximation in two different ways while retaining the simplicity of its analytic equations: First we substituted $B_v = B_e - \alpha_e(v+\frac{1}{2})$ and $\omega_e - \omega_e x_e(v+\frac{1}{2})$ for B_e and ω_e, respectively, to take into account the anharmonicity of the potential energy. However, the transposition was not removed and the results were even less accurate than those for the harmonic oscillator. Then we resorted to the variational method and used the eigenfunctions of $p^2/2\mu + \Omega^2(x-x_0)^2$ as trial functions. The variational parameters Ω and x_0 were set so that the matrix elements $\langle 0|H|1\rangle$ and $\langle 0|H|2\rangle$ of the Hamiltonian operator H with the Dunham function (3) vanish. This procedure, which is equivalent to minimizing the energy of the ground vibrational state, yields more accurate results (neglecting the continued transposition effect) than the previous approach using the same spectroscopic information.

Furthermore, numerical investigation with the Dunham function using various values of a_1 and a_2 indicated both that it is more important to take into account properly the former coefficient, and that the harmonic-oscillator approximation will yield an incorrect FCF array for all molecules. Therefore, one should consider this prospective behaviour of the FCF in the harmonic approximation when using this model in diverse spectroscopic applications. This fact is illustrated in section 3.

In a further attempt to derive accurate analytic expressions for FCF of diatomic molecules we resorted tȯ perturbation theory. The smallest order of perturbation appropriate for the anharmonic oscillator (3) is two; the perturbation parameter is $\lambda = (2B_e/\omega_e)^{1/2}$. We obtained the perturbation corrections of first and second order to the wavefunction for the case $J=0$ using standard Rayleigh–Schrödinger perturbation theory. The addition of the contributions coming from $J \neq 0$ offers no difficulty. Hutchisson [20] long ago performed such a calculation, but we discovered that he failed to take into account the terms arising from x^3 which contribute to the second-order correction to the wavefunction.

By means of computer algebra, we have derived some analytic FCF obtained from perturbation theory to second order, but the results appear too complicated to be useful. For instance, the expression for $q(0,\ 0)^{1/2}$ contains more than 300 terms as coefficient of an exponential factor when a_1 and a_2 are included in the potential-energy function of each electronic state; in the harmonic limit only one term remains. However, numerical calculation using this approximation proved useful because it shows that perturbation theory eliminates in most cases the transposition caused by the harmonic approximation. For instance, fig. 1 demonstrates that when six basis functions in the Rayleigh–Ritz calculation, corresponding approximately to second-order perturbation in the Rayleigh–Schrödinger procedure, are included in the basis set, the calculation is essentially converged to its limiting value. Of course, neither the harmonic approximation nor second-order perturbation theory is expected to yield generally reasonable results when either the FCF are too small (as in the case of HCl), i.e. $q(v',\ v'') \ll 1$, or λ is large (as in the case of H_2).

Table 1
Franck–Condon factors $q(v',\ v'')$ for the CN red system ($X\,{}^2\Sigma^+ \leftarrow A\,{}^2\Pi$). The three entries correspond, respectively, to harmonic-oscillator (with transposed array), Kratzer [7], and RKR [7] potential energies

v'	v''			
	0	1	2	3
0	4.96 (−1) 4.99 (−1) 4.94 (−1)	3.70 (−1) 3.71 (−1) 3.60 (−1)	1.15 (−1) 1.11 (−1) 1.19 (−1)	1.85 (−2) 1.74 (−2) 2.34 (−2)
1	3.24 (−1) 3.20 (−1) 3.35 (−1)	4.44 (−2) 4.56 (−1) 4.26 (−2)	3.41 (−1) 3.50 (−1) 3.18 (−1)	2.26 (−1) 2.23 (−1) 2.22 (−1)
2	1.28 (−1) 1.26 (−1) 1.26 (−1)	2.44 (−1) 2.40 (−1) 2.64 (−1)	1.16 (−2) 1.22 (−2) 1.37 (−2)	2.01 (−1) 2.10 (−1) 1.74 (−1)
3	3.92 (−2) 3.99 (−2) 3.49 (−2)	2.01 (−1) 1.95 (−1) 2.07 (−1)	1.03 (−1) 9.89 (−2) 1.20 (−1)	8.50 (−2) 9.05 (−2) 9.25 (−2)

3. Comparison with experimental data

A striking feature of the harmonic approximation is that it leads to a FCF array the values of which closely resemble those in the transpose of the actual array. (Exceptions are H_2, HCl, and O_2 for which either λ is too large or the FCF are too small; in these cases the harmonic approximation fails to provide acceptable accurate FCF.) For this reason in most cases a simple transposition of the harmonic-oscillator FCF array leads to unexpectedly accurate results. This statement is verified in table 1 in which the transposed harmonic-oscillator FCF are compared with those obtained by means of the Kratzer and RKR potentials [7]. Assuming the latter to be the most accurate, one can conclude from this table that the transposed harmonic-oscillator results are more accurate than those based on the Kratzer function. A similar conclusion applies to the other instances for which FCF obtained by means of the Kratzer potential energy are available [7].

Table 2 presents results for the experimental distribution of relative vibrational intensity in the $A\,{}^1\Pi$ system of CO excited by means of electron impact for several incident energies [21]. The relative

Table 2
Vibrational intensity distribution [21] in the $A\,{}^1\Pi$ system of CO, relative to the intensity of the transition $X\,{}^1\Sigma^+(v''=0) \rightarrow A\,{}^1\Pi(v'=2)$. HO and THO denote harmonic-oscillator and transposed harmonic-oscillator FCF arrays, respectively

v'	Incident energy (eV) [a]							HO	THO
	400	200	98	50	48	35	25		
0	0.44±0.02	0.45±0.02	0.48	0.55	0.50	0.48±0.02	0.51±0.02	0.390	0.563
1	0.87±0.02	0.89±0.02	0.91	0.94	0.92	0.95±0.03	0.94±0.02	0.952	0.961
2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.000	1.000
3	0.83±0.03	0.88±0.02	0.80	0.80	0.81	0.81±0.04	0.78±0.03	0.580	0.803
4	0.56±0.03	0.62±0.02	0.54	0.52	0.55	0.54±0.03	0.52±0.03	0.195	0.546
5	0.34±0.01	0.39±0.02	0.32	0.32	0.33	0.34±0.04	0.31±0.02	0.036	0.329
6	0.20±0.01	0.24±0.02	0.16	0.17	0.17	-	0.16±0.02	0.002	0.181

[a] Ref. [21].

transposed harmonic-oscillator FCF $q(v'=0, v'')/q(0,2)$ are in better agreement with the experimental relative intensities of the transition $X\,^1\Sigma^+(v''=0)\rightarrow A\,^1\Pi(v')$ than the appropriate relative FCF for this transition, $q(v', v''=0)/q(2,0)$. The measured relative intensities depend on the energy of the incident beam showing that other effects, in addition to the FCF, are present. For this reason one cannot use these experimental results as a criterion to decide whether one theoretical approach is better than another. However, this fact does not affect our previous conclusions because for all the incident energies considered in table 2 the relative FCF obtained from the transposed harmonic-oscillator array agree better with the experimental relative intensities than the relative FCF obtained from the non-transposed array.

4. Conclusions

We have shown that the harmonic approximation predicts misleading relative magnitudes of the off-diagonal elements of the FCF array. This behaviour, which is mainly due to the neglect of the cubic term in the expansion of the potential-energy function about its minimum, is expected to occur for most diatomic molecules. The transposition of the FCF array may lead to unexpected errors when the experimental intensities of the vibronic transitions and the geometry of the lower electronic state are used to predict the geometry of the upper electronic state. Furthermore, in most cases studied the harmonic-oscillator FCF array fortuitously by corresponds closely to the transpose of the FCF array obtained by means of more accurate and reliable approaches. For this reason the transposed array of harmonic-oscillator FCF is in remarkable agreement with experimental vibrational intensity distributions. It is of utmost importance to ascertain whether this transposition also occurs for polyatomic molecules to which the harmonic-oscillator approximation is commonly applied [12,22] because either there is insufficient information to use more accurate approaches or their implementation is difficult.

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