Vol. A58 (1980) ACTA PHYSICA POLONICA No 3

EFFECT OF FREQUENCY CHANGE OF MOLECULAR VIBRATIONS ON FRANCK–CONDON FACTORS

By A. Sobolewski

Institute of Physics, Polish Academy of Sciences, Warsaw*

(Received February 19, 1980)

The influence of frequency change in the harmonic and Morse oscillators on the vibrational Franck–Condon factors has been analysed. An oscillating behaviour of the Franck–Condon factors vs frequency change has been revealed. Some physical consequences of this fact are discussed.

1. Introduction

The overlap integral, $I_{nl,ms}$, between two vibrational wavefunctions of the harmonic oscillators χ_{ms} and χ_{nl} that describe vibrational levels m and n in the initial (s) and the final (l) electronic states, has a well-known general form [1]

$$I_{nl,ms} = \int\limits_{-\infty}^{+\infty} \chi_{nl}^{*}(Q_l)\chi_{ms}(Q_s)dQ \equiv \langle n^l|m^s\rangle. \tag{1}$$

In molecular spectroscopy, a square of integral (1), $I^2_{nl,ms}$, widely known as the Frack–Condon (FC) factor, plays a very important role in description and interpretation of many spectroscopical problems. For instance, it determines a relative distribution of the vibrational intensity in electronic spectra absorption and emission, as well as the probability of radiationless transition between electronic states of a molecule.

In the case of harmonic vibrations the FC factors between vibrationless initial state (χ_{0s}) and the manifold of the final states $\{\chi_{nl}\}$ are monotonically changing with vibrational quantum number n [1]. Recently, however, Shimakura et al. [2] have found that in the case of anharmonic vibrations the change of frequency of vibration, between the two combining electronic states, affects the FC factors in a complicated way.

In this paper we will inspect changes of the parameters of potential energy surfaces (i.e. the change of frequency and/or the shift of equilibrium geometry) on the FC factors for the harmonic as well as the anharmonic oscillators.

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* Address: Instytut Fizyki PAN, Lotników 32/46, 02-668 Warszawa, Poland.

2. *Theoretical models and the results*

2.1. Harmonic oscillator

In the majority of spectroscopical problems of practical importance, the electronic transitions are initiated from vibrationless levels in the upper (emission and/or radiationless transitions) or in the lower (absorption) electronic state. In such cases the overlap integral (1), for the harmonic oscillator, can be recasted [3] into the form

$$\langle n|0\rangle = N_n\left[\frac{\Delta}{\sqrt{2}}(1+\xi)\right]^n \sum_{s=0}^{n/2}(-1)^s\frac{n!}{s!(n-2s)!}\left[\frac{\xi}{\Delta^2(1+\xi)^2}\right]^s, \tag{2}$$

where

$$N_n = \left(\frac{\sqrt{1-\xi^2}}{n!}\right)^{1/2}\exp\left[-\frac{\Delta^2}{4}(1+\xi)\right],$$

$$\xi = \frac{\omega^s-\omega^l}{\omega^s+\omega^l},\quad \Delta = \left(\frac{u^l\omega^l}{\hbar}\right)^{1/2}(Q_0^s-Q_0^l).$$

Here, ω^s, ω^l are the vibrational frequencies, Q_0^s and Q_0^l are the equilibrium distances in the s and l electronic states, respectively, u^l is the reduced mass of the molecular vibration. The frequency change parameter, ξ, and the reduced diplacement, Δ, describe relative changes of nuclear potential energy surfaces due to the electronic transition. Both these parameters can be either positive or negative.

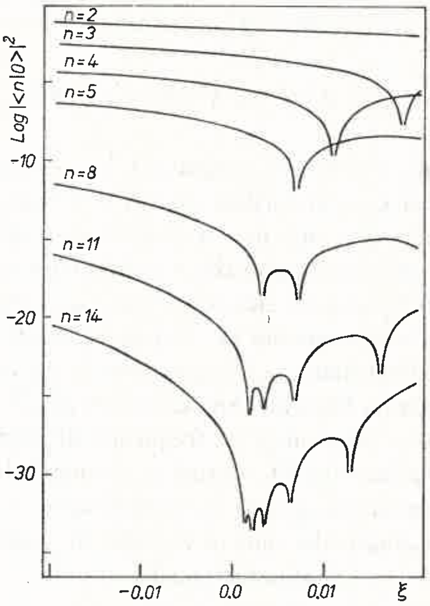

Fig. 1. Dependence of Franck–Condon factors on frequency change parameter, for different quantum numbers n of the final state, obtained according to Eq. (2) with $|\Delta| = 0.30$

Figure 1 illustrates dependence of FC factors on frequency change parameter, ξ, for different quantum numbers, n, of the final state, calculated with the aid of Eq. (2). In these calculations the reduced displacement, Δ, has been taken as being of the order of that observed for C—H totally symmetric vibrational modes in aromatic hydrocarbons [4, 5] and the frequency change parameter, ξ, has been varied within the physically motivated range. The following general conclusions can be drawn from inspection of Fig. 1:

(*i*) For $\xi \leqslant 0$, the Franck–Condon factors depend monotonically on the changes of frequency of vibration.

(*ii*) An increase in vibrational frequency in the initial state or its decrease in the final state ($\xi > 0$) affects the FC factors in a complicated way. Thus, for small quantum numbers $n < 3$ the FC factors are still changing monotonically with ξ, but for larger quantum numbers an oscillating dependence of the FC factors is observed. Furthermore, a number of oscillations in a given range of ξ grows with the increase in a quantum number.

Mathematically, the oscillating character of the FC factors comes in a natural way from the structure of Eq. (2), as the large changes of the FC factors by several orders of magnitude correspond to the roots of equation $|\langle n|0\rangle|^2 = 0$. Physical consequences of this fact will be discussed in Section 3.

2.2. Morse oscillator

In preceding discussion we have confined to the simple harmonic potential well for the nuclear motion. It is a well known fact, however, that some of molecular vibrations as for instance the C—H vibrations in aromatic hydrocarbons are significantly anharmonic [4, 6, 7]. In such cases harmonic approximation often leads to incorrect results. Hence, a more realistic model, that would incorporate anharmonicity, is needed.

Anharmonic oscillator model, most frequently utilized in a treatment of molecular vibrations, is the Morse oscillator. In this model an overlap integral $\langle n|0\rangle$ is given by [2]

$$\langle n|0\rangle = (-1)^n N_n \left(1-\frac{2n}{p}\right)^{1/2} F_n\left(\frac{p_0-p}{2}\right), \tag{3}$$

where

$$N_n = [\tfrac{1}{2}(1+f^{-1}e^{-\alpha\Delta})]^{-p_0/2}\,[\tfrac{1}{2}(1+fe^{\alpha\Delta})]^{-p/2}\left[\frac{p\Gamma(p+1-n)}{n!\Gamma(p_0)}\right]^{1/2},$$

$$p = \frac{1}{x}-1, \quad p_0 = \frac{f}{x}-1, \quad f = \frac{\omega^s}{\omega^l} = \frac{1+\xi}{1-\xi}, \quad \alpha = (2x)^{1/2},$$

and x comes, by definition, from the energy of anharmonic oscillator

$$E_n = \hbar\omega^l(n+\tfrac{1}{2}) - x\hbar\omega(n+\tfrac{1}{2})^2.$$

F_n function appearing in Eq. (3) can be derived in a form which would allow a transition from the anharmonic to the harmonic approximation under limiting condition $\alpha \to 0$

$$F_n(M) = \sum_{\sigma=0}^{n} (-1)^\sigma [\tfrac{1}{2}(fe^{\alpha\Delta}-1)]^\sigma \binom{n}{\sigma} \frac{\Gamma(M+n)\Gamma(p+M-n)}{\Gamma(M+\sigma)\Gamma(p+1-n-\sigma)}.$$

The investigation of the influence of frequency change parameter ξ, on the anharmonic FC factors, reveals basically the same behaviour as in the case of harmonic approximation. It shows, however, that the reduced displacement, Δ, and the anharmonicity parameter, α, play a very important role in governing and controlling of the FC factors. This is illustrated in Fig. 2 and can be briefly summarized as follows:

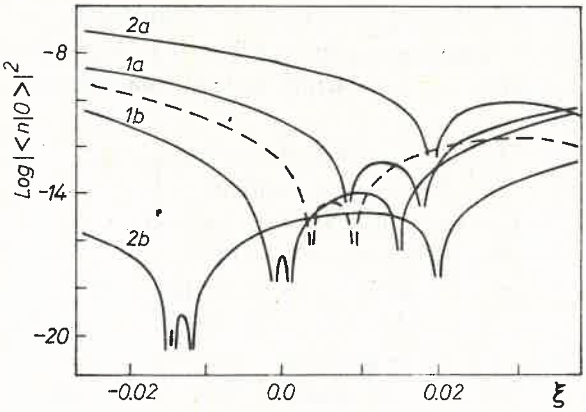

Fig. 2. Dependence of Franck–Condon factors on frequency change parameter, as given by Eq. (3) for quantum number $n = 6$ of the final state. 1a — $\Delta = -0.30$, $\alpha = 0.025$; 1b — $\Delta = 0.30$, $\alpha = 0.025$; 2a — $\Delta = -0.30$, $\alpha = 0.077$; 2b — $\Delta = 0.30$, $\alpha = 0.077$. Broken line is that for harmonic oscillator Eq. (2) with $|\Delta| = 0.30$, $n = 6$

(*i*) When $\Delta < 0$, the increase of anharmonicity, α, increases the magnitude and reduces the number of oscillations of the FC factors (number of roots of Eq. $|\langle n|0\rangle|^2 = 0$) in a given range of ξ.

(*ii*) When $\Delta > 0$, the increase of α decreases the magnitude and intensifies oscillating character of the FC factors.

(*iii*) In the limit: $\alpha \to 0$, both above cases ($\Delta < 0$ and $\Delta > 0$) merge to the harmonic approximation (in that case $|\langle n|0\rangle|^2$ is independent of the sign of Δ).

3. *Concluding remarks*

This study has revealed the oscillating character of the FC factors and has demonstrated that this feature is inherently due to the changes of the parameters determining potential energy surfaces of combined electronic states.

The oscillating character of the FC factors can drastically change their magnitude for some vibrational numbers n of the final state. Furthermore, this oscillating character can be appreciably modified by anharmonicity of a given vibration. It is obvious that these facts can have a great influence on accepting ability of molecular vibrational modes involved in radiationless transitions [1, 8]. As the energy gaps between electronic states are large, several quanta of excitation (high vibrational quantum numbers of a given accepting mode) are necessary in order to assure an effective radiationless transition. It is not surprising, in terms of our results, that some high-frequency modes, like for instance C—H vibrations in aromatic hydrocarbons active in $T_1 \rightsquigarrow S_0$ intersystem crossing [2, 4], can act as good accepting modes, and that their accepting ability can be still enhanced by anharmonicity (for C—H modes $\Delta < 0$ and anharmonicity would reduce oscillating character of the FC factors, cf. Fig. 2). On the other hand, anharmonicity of such modes like some C—C skeletal stretch $\Delta > 0$ can completely wash out their accepting ability.

Finally, we want to emphasize that although our calculations and discussion were confined to the simple $\langle n|0\rangle$ integrals, the oscillating character of the FC factors can be easily and strictly generalized for the integrals of general $\langle m|n\rangle$ type [3] as well as for wide class of physically interesting overlap integrals, like electric dipole or nuclear momentum integrals.

The author would like to express his thanks to dr J. Prochorow for many helpful discussions during preparation of this paper.

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