

An algebraic expression of the three-dimensional Franck-Condon factors and its application

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Abstract. A more general algebraic expression for the calculation of the four-mode Franck-Condon factors was derived straightforwardly on the base of the closed form expression of the Franck-Condon integrals between arbitrary multidimensional harmonic oscillators under the Duschinsky mixing effects. This new algebraic expression was applied to study the photoelectron spectra of D_2CO^+ (\tilde{A}^2B_1). Franck-Condon analyses and spectral simulations were carried out on the D_2CO^+ (\tilde{A}^2B_1) - D_2CO (\tilde{X}^1A_1) photoionization processes. The spectral simulations of vibrational structures based on the computed Franck-Condon factors are in excellent agreement with the observed spectra.

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1 Introduction

The square of the vibrational overlap integral between two electronic states is called the Franck-Condon factor (FCF). Calculations of FCFs are crucial for interpreting vibronic spectra of molecules as well as studying nonradiative processes. Recently, we have developed a new method for calculating Franck-Condon factors of multidimensional harmonic oscillators including the Duschinsky effect [1, 2]. Some explicit algebraic formulas of two-dimensional (two-, three-, and four-mode) Franck-Condon factors were derived straightforwardly by the properties of Hermite polynomials and Gaussian integrals. This new method was applied to study the photoelectron spectra of ClO_2^- , SO_2 , CH_3OO^- and so on [3–7]. Our approach is alternative to other existing ones [8–19] and has the advantages of being efficient and having

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no singular points. Accordingly, our method can be applied to any displaced-distorted-rotated harmonic oscillators and should be valuable in the studies of vibronic spectroscopy and non-radiative processes of molecules. However, up to date, an explicit algebraic form expression to calculate the three-dimensional four-mode Franck-Condon factors under the Duschinsky mixing effects has not been reported according to our knowledge.

In this work, we extended our approach to calculate three-dimensional Franck-Condon factors. An analytical expression for the calculation of the three-dimensional four-mode Franck-Condon integrals has been exactly derived. In addition, a general explicit formula of the three-dimensional Franck-Condon factors was given. As an example we present a calculation of the intensity distribution in the photoelectron spectrum of the $D_2CO^+(\tilde{A}^2B_1) - D_2CO(\tilde{X}^1A_1)$ transition of Formaldehyde.

2 Theoretical method

In Refs. [1, 2], a closed form expression for multidimensional Franck-Condon integrals between displaced distorted-rotated harmonic potential surfaces has been derived

$$\begin{aligned} \langle v''_1 \cdots v''_n | v'_1 \cdots v'_N \rangle = & \langle 0''_1 \cdots 0''_N | 0'_1 \cdots 0'_N \rangle \left(\prod_{j=1}^N (-1)^{v''_j + v'_j} (v''_j! v'_j!)^{-1/2} \right) \\ & \times \exp \left(\frac{1}{2} \boldsymbol{\sigma}''^T (\mathbf{I} - 2\mathbf{Q}) \boldsymbol{\sigma}'' + \frac{1}{2} \boldsymbol{\sigma}'^T (\mathbf{I} - 2\mathbf{P}) \boldsymbol{\sigma}' - 2\boldsymbol{\sigma}''^T \mathbf{R} \boldsymbol{\sigma}' \right) \\ & \times \frac{\partial^{v''_1 + \cdots + v''_N + v'_1 + \cdots + v'_N}}{\partial \sigma_1''^{v''_1} \cdots \partial \sigma_N''^{v''_N} \partial \sigma_1'^{v'_1} \cdots \partial \sigma_N'^{v'_N}} \\ & \times \exp \left(-\frac{1}{2} \boldsymbol{\sigma}''^T (\mathbf{I} - 2\mathbf{Q}) \boldsymbol{\sigma}'' - \frac{1}{2} \boldsymbol{\sigma}'^T (\mathbf{I} - 2\mathbf{P}) \boldsymbol{\sigma}' + 2\boldsymbol{\sigma}''^T \mathbf{R} \boldsymbol{\sigma}' \right), \quad (1) \end{aligned}$$

where

$$\langle 0''_1 \cdots 0''_N | 0'_1 \cdots 0'_N \rangle = 2^{N/2} (\det \Gamma' \Gamma'')^{1/4} (\det \mathbf{JQ})^{1/2} \exp \left(-\frac{1}{2} \boldsymbol{\delta}^T (\mathbf{I} - \mathbf{P}) \boldsymbol{\delta} \right), \quad (2)$$

and

$$\begin{pmatrix} \boldsymbol{\sigma}'' \\ \boldsymbol{\sigma}' \end{pmatrix} = \sqrt{2} \begin{pmatrix} \mathbf{I} - 2\mathbf{Q} & -2\mathbf{R} \\ -2\mathbf{R}^T & \mathbf{I} - 2\mathbf{P} \end{pmatrix}^{-1} \begin{pmatrix} -\mathbf{R}\boldsymbol{\delta} \\ (\mathbf{I} - \mathbf{P})\boldsymbol{\delta} \end{pmatrix}. \quad (3)$$

Here \mathbf{I} is an $N \times N$ unit matrix, and symmetric matrices \mathbf{P} and \mathbf{Q} and the $N \times N$ matrix \mathbf{R} are defined by

$$\mathbf{P} = \mathbf{S}\mathbf{Q}\mathbf{S}^T, \quad \mathbf{Q} = (\mathbf{1} + \mathbf{S}^T \mathbf{S})^{-1}, \quad \mathbf{R} = \mathbf{Q}\mathbf{S}^T, \quad (4)$$

with

$$\mathbf{S} = \boldsymbol{\lambda}_\omega \mathbf{J} \boldsymbol{\lambda}_{\omega'}^{-1}, \quad \boldsymbol{\lambda}_\omega = \text{diag}(\sqrt{\omega_1}, \dots, \sqrt{\omega_N}), \quad \boldsymbol{\delta} = \hbar^{-1/2} \boldsymbol{\lambda}_{\omega'} \mathbf{K}. \quad (5)$$

Let us present the explicit form of the three-dimensional four-mode FC integrals of the type $\langle v_1'', v_2'', v_3'' | v_1', 0, 0 \rangle$. Setting $\mathbf{I}-2\mathbf{Q}=\boldsymbol{\beta}$, $\mathbf{I}-2\mathbf{P}=\boldsymbol{\alpha}$, the derivative part of Eq. (1) can be written as

$$\begin{aligned}
 D \cdot P &= \frac{\partial^{v_1'}}{\partial \sigma_1^{v_1'}} \exp \left(-\frac{1}{2} \sum_{i,j=1}^3 \sigma_i' \alpha_{ij} \sigma_j' \right) \times \frac{\partial^{v_3''}}{\partial \sigma_3^{v_3''}} \exp \left(-\frac{1}{2} \beta_{33} \sigma_3''^2 + 2\sigma_3'' \sum_{j=1}^3 R_{3j} \sigma_j' \right) \\
 &\quad \times \frac{\partial^{v_2''}}{\partial \sigma_2^{v_2''}} \exp \left(-\frac{1}{2} \beta_{22} \sigma_2''^2 - \beta_{23} \sigma_2'' \sigma_3'' + 2\sigma_2'' \sum_{j=1}^3 R_{2j} \sigma_j' \right) \\
 &\quad \times \frac{\partial^{v_1''}}{\partial \sigma_1^{v_1''}} \exp \left(-\frac{1}{2} \beta_{11} \sigma_1''^2 - \beta_{12} \sigma_1'' \sigma_2'' - \beta_{13} \sigma_1'' \sigma_3'' + 2\sigma_1'' \sum_{j=1}^3 R_{1j} \sigma_j' \right) \\
 &= (-1)^{v_1''} (\beta_{11}/2)^{v_1''/2} \exp \left(-\frac{1}{2} \beta_{11} \sigma_1''^2 \right) \times \frac{\partial^{v_1'}}{\partial \sigma_1^{v_1'}} \exp \left(-\frac{1}{2} \sum_{i,j=1}^3 \sigma_i' \alpha_{ij} \sigma_j' + 2\sigma_1'' \sum_{j=1}^3 R_{1j} \sigma_j' \right) \\
 &\quad \times \frac{\partial^{v_3''}}{\partial \sigma_3^{v_3''}} \exp \left(-\frac{1}{2} \beta_{33} \sigma_3''^2 - \beta_{13} \sigma_1'' \sigma_3'' + 2\sigma_3'' \sum_{j=1}^3 R_{3j} \sigma_j' \right) \\
 &\quad \times \frac{\partial^{v_2''}}{\partial \sigma_2^{v_2''}} \left\{ \exp \left(-\frac{1}{2} \beta_{22} \sigma_2''^2 - \beta_{12} \sigma_1'' \sigma_2'' - \beta_{23} \sigma_2'' \sigma_3'' + 2\sigma_2'' \sum_{j=1}^3 R_{2j} \sigma_j' \right) \right. \\
 &\quad \left. \times H_{v_1''} \left[\sqrt{\frac{\beta_{11}}{2}} \sigma_1'' + \frac{1}{\sqrt{2\beta_{11}}} \left(\beta_{12} \sigma_2'' + \beta_{13} \sigma_3'' - \sum_{j=1}^3 2R_{1j} \sigma_j' \right) \right] \right\}, \quad (6)
 \end{aligned}$$

where use is made of the definition $H_n(x) = (-1)^n e^{x^2} (d^n/dx^n) e^{-x^2}$. Now, by employing

$$\frac{d^n}{dx^n} (f g) = \sum_{k=0}^n \binom{n}{k} f^{(n-k)} g^{(k)} \quad \text{and} \quad \frac{d}{dx} H_n(x) = 2n H_{n-1}(x),$$

Eq. (6) can be written as

$$\begin{aligned}
 D \cdot P &= (-1)^{v_1''} v_1'! v_1''! v_2''! v_3''! \exp \left(-\frac{1}{2} \sum_{i,j=1}^3 \sigma_i' \alpha_{ij} \sigma_j' - \frac{1}{2} \sum_{i,j=1}^3 \sigma_i'' \beta_{ij} \sigma_j'' + 2 \sum_{i,j=1}^3 \sigma_i'' R_{ij} \sigma_j' \right) \\
 &\quad \times \sum_{k_1=0} \dots \sum_{k_6=0} \frac{(-\beta_{12})^{k_1}}{k_1!} \frac{(-2\beta_{13})^{k_2}}{k_2!} \frac{(-2R_{11})^{k_3}}{k_3!}
 \end{aligned}$$

$$\begin{aligned}
& \times \left(\frac{(\beta_{11}/2)^{(v_1''-k_1-k_2-k_3)/2}}{(v_1''-k_1-k_2-k_3)!} H_{v_1''-k_1-k_2-k_3}(\beta_{11}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_1) \right) \\
& \times \left(\frac{(\beta_{22}/2)^{(v_2''-k_1-k_4-k_5)/2}}{(v_2''-k_1-k_4-k_5)!} H_{v_2''-k_1-k_4-k_5}(\beta_{22}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_2) \right) \\
& \times \left(\frac{(\beta_{33}/2)^{(v_2''-k_1-k_4-k_5)/2}}{(v_2''-k_1-k_4-k_5)!} H_{v_2''-k_1-k_4-k_5}(\beta_{33}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_3) \right) \\
& \times \left(\frac{(\alpha_{11}/2)^{(v_1'-k_2-k_4-k_6)/2}}{(v_1'-k_2-k_4-k_6)!} H_{v_1'-k_2-k_4-k_6}(\alpha_{11}^{-1/2}((\mathbf{E}-\mathbf{P})\boldsymbol{\delta})_1) \right). \quad (7)
\end{aligned}$$

Substituting Eq. (7) into Eq. (1), we obtain

$$\begin{aligned}
& \langle v_1'', v_2'', v_3'' | v_1', 0, 0 \rangle \\
& = \langle 0, 0, 0 | 0, 0, 0 \rangle (v_1'!)^{1/2} \prod_{j=1}^3 (-1)^{v_j''} (v_j''!)^{1/2} \\
& \times \sum_{k_1=0} \dots \sum_{k_6=0} \frac{(-\beta_{12})^{k_1}}{k_1!} \frac{(-\beta_{13})^{k_2}}{k_2!} \frac{(-2R_{11})^{k_3}}{k_3!} \frac{(-\beta_{23})^{k_4}}{k_4!} \frac{(-2R_{21})^{k_5}}{k_5!} \frac{(-2R_{31})^{k_6}}{k_6!} \\
& \times \left(\frac{(\beta_{11}/2)^{(v_1''-k_1-k_2-k_3)/2}}{(v_1''-k_1-k_2-k_3)!} H_{v_1''-k_1-k_2-k_3}(\beta_{11}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_1) \right) \\
& \times \left(\frac{(\beta_{22}/2)^{(v_2''-k_1-k_4-k_5)/2}}{(v_2''-k_1-k_4-k_5)!} H_{v_2''-k_1-k_4-k_5}(\beta_{22}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_2) \right) \\
& \times \left(\frac{(\beta_{33}/2)^{(v_2''-k_1-k_4-k_5)/2}}{(v_2''-k_1-k_4-k_5)!} H_{v_2''-k_1-k_4-k_5}(\beta_{33}^{-1/2}(\mathbf{R}\boldsymbol{\delta})_3) \right) \\
& \times \left(\frac{(\alpha_{11}/2)^{(v_1'-k_2-k_4-k_6)/2}}{(v_1'-k_2-k_4-k_6)!} H_{v_1'-k_2-k_4-k_6}(\alpha_{11}^{-1/2}((\mathbf{E}-\mathbf{P})\boldsymbol{\delta})_1) \right). \quad (8)
\end{aligned}$$

This result of Eq. (8), however, is unsuitable for computer implementation because when the factors in the Hermite polynomials such as $\alpha_{11} = 0$ ($\boldsymbol{\alpha} = \mathbf{I} - 2\mathbf{P}$), then the arguments of Hermite polynomials diverge. To circumvent this, using the definition of the Hermite polynomial, relative Franck-Condon factors (FCF) are defined as

$$FCF(v_1'', v_2'', v_3''; v_1', v_2', v_3') = \left| \frac{\langle v_1'', v_2'', v_3'' | v_1', v_2', v_3' \rangle}{\langle 0, 0, 0 | 0, 0, 0 \rangle} \right|^2. \quad (9)$$

By means of Eq. (8), we obtained the computational formula of FCFs for the three-dimensional

four-mode case

$$FCF(v_i, v_j, v_k, v_l) = \frac{v_i! v_j! v_k! v_l!}{2^{v_i+v_j+v_k+v_l}} \left(\sum_{k_1} \cdots \sum_{k_6} \sum_{m_1} \cdots \sum_{m_4} \right. \\ \times \frac{2^{k_1+k_2+k_4} C_{ij}^{k_1} C_{ik}^{k_2} E_{il}^{k_3} C_{jk}^{k_4} E_{jl}^{k_5} E_{kl}^{k_6} C_{ii}^{m_1} C_{jj}^{m_2} C_{kk}^{m_3} A_{ll}^{m_4}}{\prod_{\beta=1}^6 (k_\beta!) \times \prod_{\gamma=1}^4 (m_\gamma!)} \\ \times \frac{D_i^{v_i-2m_1-k_1-k_2-k_3} D_j^{v_j-2m_2-k_1-k_4-k_5}}{(v_i-2m_1-k_1-k_2-k_3)! (v_j-2m_2-k_1-k_4-k_5)!} \\ \left. \times \frac{D_k^{v_k-2m_3-k_2-k_4-k_6} B_j^{v_l-2m_4-k_5-k_6-k_3}}{(v_k-2m_3-k_2-k_4-k_6)! (v_l-2m_4-k_5-k_6-k_3)!} \right)^2, \quad (10)$$

where $\mathbf{A}, \mathbf{B}, \mathbf{C}, \mathbf{D}$ and \mathbf{E} are defined by $\mathbf{A} = -(\mathbf{I} - 2\mathbf{P})$, $\mathbf{B} = 2(\mathbf{I} - \mathbf{P})\boldsymbol{\delta}$, $\mathbf{C} = -(\mathbf{I} - 2\mathbf{Q})$, $\mathbf{D} = -2\mathbf{R}\boldsymbol{\delta}$ and $\mathbf{E} = 4\mathbf{R}$, respectively. The multiple, nested summation form is not only easily coded and evaluated by computer, but also removes the diverging values of the Hermite polynomials in Eq. (8).

3 Example for an application

As an example we present a calculation of the intensity distribution in the photoelectron spectrum of the $D_2CO^+(\tilde{A}^2B_1) - D_2CO(\tilde{X}^1A_1)$ transition of Formaldehyde, which has been studied in great detail in previous experimental and theoretical works [20–24]. First, to obtain the structure data and the force constants data which are needed to make Duschinsky's \mathbf{J} matrix and \mathbf{K} vector [4], we used the nonempirical molecular orbital method program, Gaussian03 [25].

The optimized geometric parameters and computed vibrational frequencies for the \tilde{X}^1A_1 state of D_2CO and \tilde{A}^2B_1 state of D_2CO^+ obtained at the CASSCF level in this work are applied, respectively. \mathbf{J} matrix and \mathbf{K} vector in terms of the Gaussian03 output for the two electronic states are given by [4]

$$\mathbf{J} = (M(g03')V'^{-1/2})^\dagger Z(g03'')V''^{-1/2}, \quad (11)$$

and

$$\mathbf{K} = (M(g03')V'^{-1/2})^\dagger (ZR''_{eq} - R'_{eq}). \quad (12)$$

Finally, the Duschinsky matrix and geometrical displacement vector are obtained

$$\mathbf{J} = \begin{bmatrix} 0.991 & 0.003 & -0.013 & 0 & 0 & 0 \\ -0.020 & 0.744 & -0.676 & 0 & 0 & 0 \\ 0.010 & 0.667 & 0.733 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.990 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.998 & 0.078 \\ 0 & 0 & 0 & 0 & -0.074 & -0.998 \end{bmatrix}, \quad \mathbf{K} = \begin{bmatrix} 0.007 \\ 0.317 \\ 0.130 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (13)$$

where \mathbf{K} is in units of $\text{amu}^{1/2} \text{ \AA}$. \mathbf{J} describes the mixing of normal modes. Then, according to the method of the present paper, FCF calculations on the $\tilde{A}^2B_1 - \tilde{X}^1A_1$ photoionization were carried out. The computed FCFs were used to simulate the vibrational structure of the $\tilde{A}^2B_1 - \tilde{X}^1A_1$ photoionization spectrum of D_2CO , employing a Gaussian line-shape and a full-width-at-half-maximum (FWHM) of 130 cm^{-1} for the $D_2CO^+ (\tilde{A}^2B_1) - D_2CO (\tilde{X}^1A_1)$ photoionization.

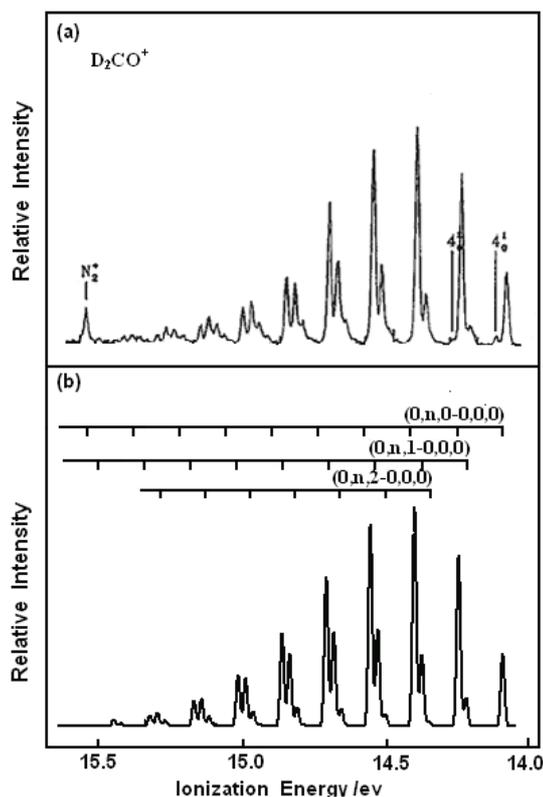


Figure 1: (a) The experimental photoelectron spectrum of D_2CO (from Ref. [5]), and (b) the simulated spectrum employing the ab initio force constants and geometry for $D_2CO^+ (\tilde{A}^2B_1)$ and the neutral $D_2CO (\tilde{X}^1A_1)$ with vibrational assignments provided for the $D_2CO^+ (\tilde{A}^2B_1) - D_2CO (\tilde{X}^1A_1)$ photoionization process. The FWHM used for the components of the simulated spectrum is 130 cm^{-1} .

The simulated photoelectron spectrum of the $D_2CO^+ (\tilde{A}^2B_1) - D_2CO (\tilde{X}^1A_1)$ photoionization is shown in Fig. 1(b), with the experimental observed photoelectron spectrum shown in Fig. 1(a). Vibrational assignments for the symmetric CO stretching ω_2 and CD_2 scissor ω_3 modes of the molecular ion D_2CO^+ are also provided with the labels $(0,n,0-0,0,0)$, $(0,0,n-0,0,0)$, $(0,n,1-0,0,0)$, $(0,n,2-0,0,0)$, $(0,n,3-0,0,0)$ corresponding to the $(0,\omega_2,\omega_3-0,0,0)$ transition. From the harmonic calculation, it was found that the FCFs for transitions involv-

ing the other modes of D_2CO^+ are negligibly small and therefore they were not included in the assignments. The relative intensities were chosen to match the second PE bands between 14.0 and 15.5 eV in the experimental spectrum [5]. It was found that the computed photoelectron spectrum of D_2CO for the $D_2CO^+ (\tilde{A}^2B_1) - D_2CO (\tilde{X}^1A_1)$ photoionization is almost identical to the experimental spectrum. However, discrepancies between simulation and observation become larger for peaks with higher quantum numbers due to anharmonicity effects not included in the FCF calculations.

4 Conclusions

An explicit algebraic expression has been derived to calculate the three-dimensional four-mode Franck-Condon factors between displaced distorted-rotated harmonic potential surfaces. This equation is exact for harmonic systems, no approximation whatsoever having been introduced in its derivation. Our method is general, in contrast to previous works in which exact FCF were obtained for very special cases by performing a finite series expansion, or approximate expressions by making use of the contact transformation perturbation methods. Practical calculations of Franck-Condon factors using the new formula for the intensity distribution in the photoelectron spectrum of the $\tilde{A}^2B_1 - \tilde{X}^1A_1$ transition of D_2CO were carried out. The spectral simulations of vibrational structures based on the computed Franck-Condon factors are in excellent agreement with the observed spectrum.

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