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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 $D_2CO^+(\widetilde{A}\ ^2B_1)$. Franck-Condon analyses and spectral simulations were carried out on the $D_2CO^+(\widetilde{A}\ ^2B_1)$ - $D_2CO(\widetilde{X}\ ^1A_1)$ 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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Key words: overlap integral, Franck-Condon factor, duschinsky effect, spectral simulation

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 $D_2CO^+(\widetilde{A}^2B_1)$ – $D_2CO(\widetilde{X}^1A_1)$ 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

$$\begin{aligned}\left\langle v_1''\cdots v_n''\middle|v_1'\cdots v_N'\right\rangle =& \left\langle 0_1''\cdots 0_N''\middle|0_1'\cdots 0_N'\right\rangle \left(\prod_{j=1}^{N}(-1)^{v_j''+v_j'}(v_j''!v_j'!)^{-1/2}\right)\\ &\times \exp\left(\frac{1}{2}\boldsymbol{\sigma}''^T(\mathbf{I}-2\mathbf{Q})\boldsymbol{\sigma}''+\frac{1}{2}\boldsymbol{\sigma}'^T(\mathbf{I}-2\mathbf{P})\boldsymbol{\sigma}'-2\boldsymbol{\sigma}''^T\mathbf{R}\boldsymbol{\sigma}'\right)\\ &\times \frac{\partial^{v_1''+\cdots+v_N''+v_1'+\cdots v_N'}}{\partial\sigma_1''^{v_1''}\cdots\partial\sigma_N''^{v_N''}\partial\sigma_1'^{v_1'}\cdots\partial\sigma_N'^{v_N'}}\\ &\times \exp\left(-\frac{1}{2}\boldsymbol{\sigma}''^T(\mathbf{I}-2\mathbf{Q})\boldsymbol{\sigma}''-\frac{1}{2}\boldsymbol{\sigma}'^T(\mathbf{I}-2\mathbf{P})\boldsymbol{\sigma}'+2\boldsymbol{\sigma}''^T\mathbf{R}\boldsymbol{\sigma}'\right),\end{aligned} \tag{1}$$

where

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

and

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

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

$$\mathbf{P}=\mathbf{SQS}^T, \qquad \mathbf{Q}=(1+\mathbf{S}^T\mathbf{S})^{-1}, \qquad \mathbf{R}=\mathbf{QS}^T, \tag{4}$$

with

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