

# Vibrationally-resolved electronic spectra in GAUSSIAN 09

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## General overview

In a first approximation level, electronic spectra (UV-vis, photoelectron, X-ray, etc.) can be simulated by computing vertical excitation energies at geometrical structures optimized for the ground electronic state, with the resulting stick spectra subsequently convoluted by Gaussian or Lorentzian functions. However, such a treatment neglects completely dynamic effects, which influence significantly the spectrum line-shape in many cases. To overcome this limitation, a new procedure to compute vibrationally-resolved electronic spectra has been included in GAUSSIAN. It relies on the Franck-Condon principle [1, 2] to evaluate the intensities of transitions between two vibronic states. This is done by considering that the nuclear positions are mostly unaltered by the electron jump which takes place during the electronic transition.

To deal with medium-to-large systems, an efficient *prescreening* scheme [3, 4] is used to choose the most relevant transitions. It is designed to be fast and simple enough to have little incidence on the computational cost of the spectrum generation, while providing an accurate choice of the transitions to deal with in order to produce accurate spectra. One of its main features is that it relies on the number of integrals to compute and not on the dimensionality of the system. As a consequence, GAUSSIAN can be tailored to perform fast calculations while retaining the general shape of the spectrum at first, as shown on figure 1. It is noteworthy that this *prescreening* scheme works as a black-box procedure and performs a full dimensional treatment, considering all vibrational modes of the studied system.

Additionally, GAUSSIAN accepts a wide range of settings to adjust the calculations or to modify the layout of the spectrum when needed. Because calculations to generate the theoretical spectrum are independent on the lower and upper bound of the latter, the energy range on which the simulation is performed has a very little impact on the computational costs<sup>1</sup>

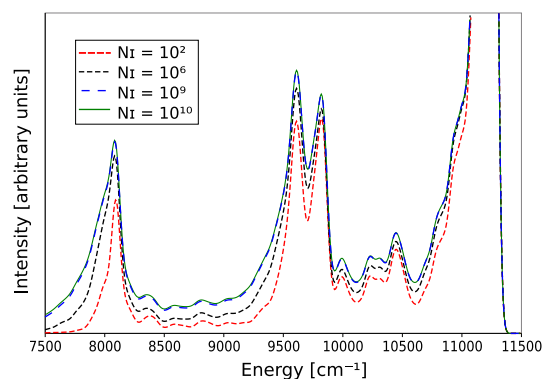


Figure 1: Convergence of the phosphorescence spectrum for chlorophyll *c2* with different maximum number of integrals to compute ( $N_I$ ) for each *class*.

<sup>1</sup>However, a high resolution, given by a small interval between two measuring points of the discretized spectrum, associated to a broad band can noticeably slow down the calculations.

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## 1 Introduction

In this new release of GAUSSIAN, it is possible to compute vibrationally-resolved absorption and emission spectra. This white paper aims at introducing the general theory underlying such calculations and presenting the possibilities offered to generate electronic spectra inside GAUSSIAN.

The document is divided as follows. After a brief introduction of the basic theory used in GAUSSIAN to generate vibronic spectra, a quick presentation of its basic usage is given. The main features of the input and output will then be described. The second part of the document is devoted to more advanced cases and to the tools to control and fine-tune the calculations to meet specific needs. The available options and their purpose will be listed, followed by examples of applications showing the usage of the most common ones. The last part summarizes the most common errors reported by GAUSSIAN and possible workarounds. This section is not aimed at being exhaustive and alternative solutions can work as well or even be more adapted to some particular cases.

The following typographic conventions will be used thereafter:

- ' : placed next to a letter/symbol, refers to the initial state
- " : placed next to a letter/symbol, refers to the final state
- $N_A$  : represents the number of atoms in the molecule or system of interest
- $N$  : represents the number of normal modes in the molecule or system of interest
- $M$  : designates a matrix or vector
- $M_i$  or  $M(i)$  : represents the  $i$ -th element of vector  $M$
- $M_{ij}$  or  $M(i, j)$  : represents the  $i, j$  element of matrix  $M$

*Note:* For convenience, the notation adopted in this document is slightly different from the spectroscopic conventions since the relative energies of the initial and final states are not taken into account when using ' and ". This allows to treat indifferently the similar cases of absorption and emission without duplicating the formulae.

## 2 Theoretical background

The theoretical description in this section is not intended to be exhaustive but rather to give a sufficient background in order to use GAUSSIAN for the simulation of vibrationally resolved electronic spectra. It is divided in three subsections. The first one presents a general theoretical background and the approximations used to compute the transition dipole moment and the transition intensities. This will help to understand the possibilities given by the Franck-Condon principle as well as the limit of such a method. The second part deals with the prescreening method used by GAUSSIAN to choose *a priori* the most intense transitions. The parameters on which it relies as well as their influence are described there. Finally, a discussion on the guessing of spectrum convergence is carried out.

## Calculation of the transition dipole moment

Line intensities in one-photon absorption and emission spectra depend on the square of the transition dipole moment  $\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle$  as well as on the radiation frequency ( $\omega$ )<sup>2</sup>:

$$\sigma(\omega)_{\text{abs}} = \frac{4\pi^2\omega}{3c} \sum' \rho' \sum'' |\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle|^2 \delta(E'' - E' - \hbar\omega) \quad (1)$$

$$\sigma(\omega)_{\text{emi}} = \frac{4\omega^3}{3\hbar c^3} \sum' \rho' \sum'' |\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle|^2 \delta(E'' - E' + \hbar\omega) \quad (2)$$

where  $\rho'$  is the Boltzmann population of each initial state and  $\sigma(\omega)$  is the rate of photon absorption (or emission) per molecule and per unit of radiant energy.  $\Psi'$  and  $\Psi''$  represent the molecular wave functions of the initial and final state, respectively:

In the frame of the Born-Oppenheimer approximation, it is possible to write the molecular wave function  $\Psi$  as a product of an electronic wave function  $\psi_e$  and a nuclear wave function  $\psi_n$ . The transition dipole moment can then be written,

$$\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle = \langle \psi'_e \psi'_n | \boldsymbol{\mu}_e | \psi''_e \psi''_n \rangle + \langle \psi'_e \psi'_n | \boldsymbol{\mu}_n | \psi''_e \psi''_n \rangle \quad (3)$$

Since the electronic wave functions are orthogonal to each other, the second term of the rhs in the previous equation vanishes.

We further assume that the Eckart conditions [5] are met, so that the nuclear wave function can be, with a good approximation, separated into a rotation and a vibrational contribution, the translational part being completely separated from the other two and discarded here. In the treatment presented here, rotational energies are considered sufficiently small and will not be taken into account.

Using both approximations, the transition dipole moment can finally be written,

$$\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle \approx \langle \psi'_v | \boldsymbol{\mu}_{if} | \psi''_v \rangle \quad (4)$$

where  $\boldsymbol{\mu}_{if} = \langle \psi'_e | \boldsymbol{\mu} | \psi''_e \rangle$  is the electronic transition dipole moment.

In the method implemented in GAUSSIAN, the harmonic approximation is also used. As a consequence, it is possible to write the multidimensional vibrational wave function  $\psi_v$  as a product of monodimensional wave functions  $\psi_{v_i}(Q_i)$ , where  $Q_i$  is one of the  $N$  normal coordinates, describing the  $i$ -th vibration of the molecule.

However, since the analytic form of the electronic transition dipole moment is unknown, these approximations are not yet sufficient to compute the transition dipole moment. An additional approximation is done by using the Franck-Condon principle, proposed by Franck [1] and mathematically formalized by Condon [2]. The underlying theory is that, during a transition, the electron jump in a molecule takes place in such a short time that the relative positions and velocities of the nuclei are nearly unaltered by the molecular vibrations. Following this principle, schematically shown in figure 2, the most intense transition will be from the chosen initial state to a final state being at a minimum of the lowest potential surface vertically upward. Since this approximation is very restrictive by assuming that the electronic transition dipole moment remains constant during the transition, a more flexible approach is adopted here. Indeed, since the shifts of the nuclear positions in the molecule are often fairly small during the electronic transition, it is possible, with a good accuracy, to develop the electronic transition dipole moment in a Taylor series about the equilibrium geometry of one state of reference, which is the final state in our case:

$$\boldsymbol{\mu}_{if}(\mathbf{Q}'') \simeq \boldsymbol{\mu}_{if}(\mathbf{Q}_0'') + \sum_{k=1}^N \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q_k''} \right)_0 Q_k'' + \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N \left( \frac{\partial^2 \boldsymbol{\mu}_{if}}{\partial Q_k'' \partial Q_l''} \right)_0 Q_k'' Q_l'' + \dots \quad (5)$$

where  $\mathbf{Q}_0''$  represents the equilibrium geometry of the final state.

<sup>2</sup>With respect to the formulae presented here, GAUSSIAN does not take into account the constant part to calculate the intensity of the spectrum lines

The zeroth order term corresponds to a static electronic transition dipole. This is a direct application of the Franck-Condon principle mentioned above. As a consequence, it is referred as the Franck-Condon (FC) approximation. When dealing with fully-allowed transitions ( $|\mu_{if}(\mathbf{Q}_0'')| \gg 0$ ), this approximation generally gives very good results.

However, in the case of weakly-allowed ( $|\mu_{if}(\mathbf{Q}_0'')| \sim 0$ ) or dipole-forbidden ( $|\mu_{if}(\mathbf{Q}_0'')| = 0$ ) electronic transitions, this approximation is not describing correctly the overall spectrum, missing the most intense vibronic transitions. It is necessary to consider a variation of the dipole moment during the transition. A first approximation is to account for a linear variation of the dipole moment with the normal coordinates. This corresponds to the first order of the Taylor expansion and is referred as the Herzberg-Teller [6] (HT) approximation<sup>3</sup>. Hereafter, the FC approximation considers only the first term in the rhs of eq. 5, HT the second one, and FCHT both terms, as approximation of  $\mu_{if}$ .

Using eq. 5, the transition dipole moment can be written:

$$\begin{aligned} \langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle &= \boldsymbol{\mu}_{if}(\mathbf{Q}_0'') \langle \psi'_v | \psi''_v \rangle \\ &+ \sum_{k=1}^N \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q_k''} \right)_0 \langle \psi'_v | Q_k'' | \psi''_v \rangle \\ &+ \frac{1}{2} \sum_{k=1}^N \sum_{l=1}^N \left( \frac{\partial^2 \boldsymbol{\mu}_{if}}{\partial Q_k'' \partial Q_l''} \right)_0 \langle \psi'_v | Q_k'' Q_l'' | \psi''_v \rangle \end{aligned} \quad (6)$$

The overlap integral  $\langle \psi'_v | \psi''_v \rangle$  is also referred to as the Franck-Condon integral. The integrals in the second and third terms of equation 5 depend on the normal coordinates and therefore cannot be, in this form, generalized to any problem. To simplify the calculation of the integrals given in equation 6, it is necessary to transform them in more versatile and usable Franck-Condon integrals. This is done by using the creation and annihilation operators from the second quantization, respectively  $a_i^\dagger$  and  $a_i$ , defined as

$$a_i^\dagger = \sqrt{\frac{\omega_i}{2\hbar}} \left( Q_i - \frac{d}{dQ_i} \right) \quad (7)$$

$$a_i = \sqrt{\frac{\omega_i}{2\hbar}} \left( Q_i + \frac{d}{dQ_i} \right) \quad (8)$$

Hence,

$$Q_i = \left( \frac{\hbar}{2\omega_i} \right)^{1/2} [a_i + a_i^\dagger] \quad (9)$$

In the current implementation, the Taylor expansion of the electronic transition dipole moment is supported up to the second term in the rhs in eq. 5. As a consequence, the approximation of  $\mu_{if}$  will be limited to the Franck-Condon and Herzberg-Teller terms. In addition, the vibrational wave function will be replaced from now on by a vector “ $\mathbf{v}$ ” containing the quantum numbers  $v_i$  representing the same vibrational state described by  $\psi_v$ :

$$| \mathbf{v} \rangle = | \psi_v \rangle = \left| \prod_{i=1}^N \psi_{v_i} \right\rangle$$

Using eq. 9, the second term integral in the rhs of eq. 6 can be rewritten,

$$\langle \mathbf{v}' | Q_k'' | \mathbf{v}'' \rangle = \sqrt{\frac{\hbar}{2\omega_k''}} \left[ \sqrt{v_k''} \langle \mathbf{v} | \mathbf{v}'' - 1_k'' \rangle + \sqrt{v_k'' + 1} \langle \mathbf{v} | \mathbf{v}'' + 1_k'' \rangle \right] \quad (10)$$

<sup>3</sup>In their original work, Herzberg and Teller considered the initial state as the state of reference for the linear variation of the electronic transition dipole moment. We use here a more general interpretation of their work by applying to any state of reference.

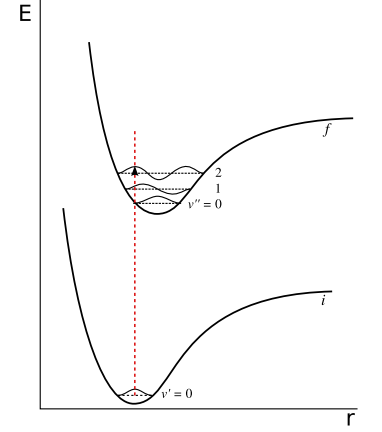


Figure 2: The Franck-Condon principle is shown by the vertical dotted line. Following this principle, the highest probability of transition corresponds to  $\langle \mathbf{0}' | \mathbf{2}'' \rangle$  where the overlap of the wave functions is the highest.

where  $|\mathbf{v}'' + 1''_i\rangle$  represents, from the energy perspective, a vibrational state which differs from the state represented by  $|\mathbf{v}''\rangle$  by the eigenvalue of the monodimensional Schrödinger equation  $E_{v''_i+1} = \hbar\omega''_i(v''_i + 1/2) = E_{v''_i} + \hbar\omega''_i$ .

Inserting eq. 10 in eq. 6, it is possible to write the transition dipole moment integral as a combination of overlap integrals:

$$\begin{aligned} \langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle = & \boldsymbol{\mu}_{if}(\mathbf{Q}''_0) \langle \mathbf{v}' | \mathbf{v}'' \rangle \\ & + \sum_{k=1}^N \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q''_k} \right)_0 \sqrt{\frac{\hbar}{2\omega''_k}} \left[ \sqrt{v''_k} \langle \mathbf{v}' | \mathbf{v}'' - 1''_k \rangle \right. \\ & \left. + \sqrt{v''_k + 1} \langle \mathbf{v}' | \mathbf{v}'' + 1''_k \rangle \right] \end{aligned} \quad (11)$$

The overlap integrals are given by the equation,

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle = & \pi^{-N/2} \det[\boldsymbol{\Gamma}' \boldsymbol{\Gamma}'' ]^{1/4} \det(\mathbf{J})^{1/2} \left( \prod_{i=1}^N 2^{v'_i} 2^{v''_i} (v'_i!) (v''_i!) \right)^{-1/2} \\ & \times \int_{-\infty}^{+\infty} dQ''_1 \dots dQ''_N \left( \prod_{i=1}^N H_{v'_i}(\boldsymbol{\Gamma}'^{1/2} Q'_i) H_{v''_i}(\boldsymbol{\Gamma}''^{1/2} Q''_i) \right) \\ & \times \exp \left[ -\frac{1}{2} (\mathbf{Q}'^T \boldsymbol{\Gamma}' \mathbf{Q}' + \mathbf{Q}''^T \boldsymbol{\Gamma}'' \mathbf{Q}'') \right] \end{aligned} \quad (12)$$

where  $\boldsymbol{\Gamma}'$  and  $\boldsymbol{\Gamma}''$  are the diagonal matrices of the reduced frequencies from the initial and final states, respectively, and  $H_{v_i}(q_i)$  is a Hermite polynomial of degree  $v_i$  defined by:

$$H_{v_i}(q_i) = (-1)^{v_i} e^{q_i^2} \frac{d^{v_i}}{dq_i^{v_i}} e^{-q_i^2} \quad (13)$$

A first issue to calculate the integral in eq. 12 arises from the fact that each vibrational wave function is expressed in a different set of normal coordinates. To overcome this, the linear transformation proposed by Duschinsky [7] to express the normal coordinates of one state with respect to the other's is used,

$$\mathbf{Q}' = \mathbf{J} \mathbf{Q}'' + \mathbf{K} \quad (14)$$

where  $\mathbf{J}$  is called the Duschinsky matrix and represents the mixing of the normal modes during the transition, and  $\mathbf{K}$  is the shift vector due to the changes in geometry between the initial and final states. This transformation is generally a good approximation, when the molecule does not undergo a noticeable distortion during the transition.

The rotation or Duschinsky matrix and shift vector are given by:

$$\mathbf{J} = (\mathbf{L}')^{-1} \mathbf{L}'' \quad (15)$$

$$\mathbf{K} = (\mathbf{L}')^{-1} \mathbf{M}^{1/2} \boldsymbol{\Delta} \mathbf{X} \quad (16)$$

where  $\mathbf{L}'$  and  $\mathbf{L}''$  are the transformation matrices from mass-weighted Cartesian coordinates to normal coordinates,  $\mathbf{M}$  is the diagonal matrix of atomic masses and  $\boldsymbol{\Delta} \mathbf{X}$  is a vector representing the shift of nuclear Cartesian coordinates between the initial and final states.

$\mathbf{J}$  and  $\mathbf{K}$  can be printed in GAUSSIAN with the keyword `PrTMat` in the *ReadFCHT* section (with the respective values 1 and 2 as shown in the keywords list).

In addition, while the overlap integral between the vibrational ground states  $\langle \mathbf{0}' | \mathbf{0}'' \rangle$  can be straightforwardly calculated, this is generally not the case for  $\langle \mathbf{v}' | \mathbf{v}'' \rangle$  where  $\mathbf{v}'$  and/or  $\mathbf{v}''$  are not null. Among the several computational approaches proposed till now, we have selected the Sharp and Rosenstock's one [8]. However, their original work was based on analytic formulae for each possible combination of  $\mathbf{v}'$  and  $\mathbf{v}''$  and it is not adapted when dealing with a large number of normal modes. A more versatile method based on recursive formulae [9], which follows a similar formalism is described here.

First, two dummy vectors,  $\mathbf{T}$  and  $\mathbf{U}$ , are defined to be near-null so that,

$$H_{\mathbf{v}'}(\mathbf{\Gamma}'^{1/2}\mathbf{Q}') = \left( \frac{\partial^{v'}}{\partial \mathbf{T}^{v'}} \exp[-\mathbf{T}^2 + 2\mathbf{T}^T \mathbf{\Gamma}'^{1/2} \mathbf{Q}'] \right)_{\mathbf{T}=\mathbf{0}} \quad (17)$$

and

$$H_{\mathbf{v}''}(\mathbf{\Gamma}''^{1/2}\mathbf{Q}'') = \left( \frac{\partial^{v''}}{\partial \mathbf{U}^{v''}} \exp[-\mathbf{U}^2 + 2\mathbf{U}^T \mathbf{\Gamma}''^{1/2} \mathbf{Q}''] \right)_{\mathbf{U}=\mathbf{0}} \quad (18)$$

where

$$\frac{\partial^{v''}}{\partial \mathbf{U}^{v''}} = \frac{\partial^{v''_1}}{\partial U_1^{v''_1}} \frac{\partial^{v''_2}}{\partial U_2^{v''_2}} \cdots \frac{\partial^{v''_N}}{\partial U_N^{v''_N}} \quad \text{and} \quad \frac{\partial^{v'}}{\partial \mathbf{T}^{v'}} = \frac{\partial^{v'_1}}{\partial T_1^{v'_1}} \frac{\partial^{v'_2}}{\partial T_2^{v'_2}} \cdots \frac{\partial^{v'_N}}{\partial T_N^{v'_N}} \quad (19)$$

Replacing the Hermite polynomials in eq. 12 by their definitions given in eqs. 17 and 18, and using the Duschinsky transformation, the following formula is obtained:

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle &= \pi^{-N/2} \det[\mathbf{\Gamma}' \mathbf{\Gamma}'']^{1/4} \det(\mathbf{J})^{1/2} \left( 2^{v'} 2^{v''} \mathbf{v}'! \mathbf{v}''! \right)^{-1/2} \\ &\times \left( \frac{\partial^{v'}}{\partial \mathbf{T}^{v'}} \frac{\partial^{v''}}{\partial \mathbf{U}^{v''}} \exp[-\mathbf{T}^2 - \mathbf{U}^2] \int d\mathbf{Q}'' \exp \left[ \frac{1}{2} (\mathbf{Q}''^T \mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} \mathbf{Q}'' \right. \right. \\ &\quad \left. \left. + \mathbf{Q}''^T \mathbf{J}^T \mathbf{\Gamma}' \mathbf{K} + \mathbf{K}^T \mathbf{\Gamma}' \mathbf{J} \mathbf{Q}'' + \mathbf{K}^T \mathbf{\Gamma}' \mathbf{K} + \mathbf{Q}''^T \mathbf{\Gamma}'' \mathbf{Q}'' \right) \right. \\ &\quad \left. + 2\mathbf{U}^T \mathbf{\Gamma}''^{1/2} \mathbf{Q}'' + 2\mathbf{T}^T \mathbf{\Gamma}'^{1/2} \mathbf{J} \mathbf{Q}'' + 2\mathbf{T}^T \mathbf{\Gamma}'^{1/2} \mathbf{K} \right] \Bigg|_{\mathbf{T}=\mathbf{U}=\mathbf{0}} \end{aligned} \quad (20)$$

After developing and integrating the previous equation, we obtain:

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle &= \left( 2^{v'} 2^{v''} \mathbf{v}'! \mathbf{v}''! \right)^{-1/2} \frac{\partial^{v'}}{\partial \mathbf{T}^{v'}} \frac{\partial^{v''}}{\partial \mathbf{U}^{v''}} 2^{N/2} \det[\mathbf{\Gamma}' \mathbf{\Gamma}'']^{1/4} \left[ \frac{\det(\mathbf{J})}{\det(\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')} \right]^{1/2} \\ &\times \exp \left[ -\frac{1}{2} \mathbf{K}^T \mathbf{\Gamma}' \mathbf{K} + \frac{1}{2} \mathbf{K}^T \mathbf{\Gamma}' \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}' \mathbf{K} \right] \\ &\times \exp \left[ \mathbf{U}^T (2\mathbf{\Gamma}''^{1/2} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{\Gamma}''^{1/2} - \mathbf{I}) \mathbf{U} \right] \\ &\times \exp \left[ -2\mathbf{K}^T \mathbf{\Gamma}' \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{\Gamma}''^{1/2} \mathbf{U} \right] \\ &\times \exp \left[ \mathbf{T}^T (2\mathbf{\Gamma}'^{1/2} \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}'^{1/2} - \mathbf{I}) \mathbf{T} \right] \\ &\times \exp \left[ -2\mathbf{K}^T (\mathbf{\Gamma}' \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T - \mathbf{I}) \mathbf{\Gamma}'^{1/2} \mathbf{T} \right] \\ &\times \exp \left[ \mathbf{U}^T 4\mathbf{\Gamma}''^{1/2} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}'^{1/2} \mathbf{T} \right] \end{aligned} \quad (21)$$

To simplify the notation, 5 matrices referred to hereafter as Sharp and Rosenstock matrices are defined:

$$\begin{aligned} \mathbf{A} &= 2\mathbf{\Gamma}'^{1/2} \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}'^{1/2} - \mathbf{I} \\ \mathbf{B} &= -2\mathbf{\Gamma}'^{1/2} (\mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}' - \mathbf{I}) \mathbf{K} \\ \mathbf{C} &= 2\mathbf{\Gamma}''^{1/2} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{\Gamma}''^{1/2} - \mathbf{I} \\ \mathbf{D} &= -2\mathbf{\Gamma}''^{1/2} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}' \mathbf{K} \\ \mathbf{E} &= 4\mathbf{\Gamma}''^{1/2} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}'^{1/2} \end{aligned}$$

These matrices can also be printed in GAUSSIAN with the keyword PrtMat in the *ReadFCHT* section (with the respective values 3, 4, 5, 6 and 7 as shown in the keywords list).

In addition, setting  $\mathbf{v}' = \mathbf{v}'' = \mathbf{0}$ , we obtain from eq. 21 the overlap integral between the vibrational ground states:

$$\begin{aligned} \langle \mathbf{0}' | \mathbf{0}'' \rangle &= 2^{N/2} \det[\mathbf{\Gamma}' \mathbf{\Gamma}'' ]^{1/4} \left[ \frac{\det(\mathbf{J})}{\det(\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')} \right]^{1/2} \\ &\times \exp \left[ -\frac{1}{2} \mathbf{K}^T \mathbf{\Gamma}' \mathbf{K} + \frac{1}{2} \mathbf{K}^T \mathbf{\Gamma}' \mathbf{J} (\mathbf{J}^T \mathbf{\Gamma}' \mathbf{J} + \mathbf{\Gamma}'')^{-1} \mathbf{J}^T \mathbf{\Gamma}' \mathbf{K} \right] \end{aligned} \quad (22)$$

Hence, eq. 21 can be written,

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle &= \left( 2^{v'_i} 2^{v''_i} v'_i! v''_i! \right)^{-1/2} \left( \frac{\partial^{v'_i}}{\partial \mathbf{T}^{v'_i}} \frac{\partial^{v''_i}}{\partial \mathbf{U}^{v''_i}} \langle \mathbf{0}' | \mathbf{0}'' \rangle \right. \\ &\left. \times \exp \left[ \mathbf{U}^T \mathbf{C} \mathbf{U} + \mathbf{D}^T \mathbf{U} + \mathbf{T}^T \mathbf{A} \mathbf{T} + \mathbf{B}^T \mathbf{T} + \mathbf{U}^T \mathbf{E} \mathbf{T} \right] \right)_{\mathbf{T}=\mathbf{U}=\mathbf{0}} \end{aligned} \quad (23)$$

This equation is the starting point to generate two recursive formulae depending on the initial differentiation, with respect to  $\mathbf{T}_i$  or  $\mathbf{U}_i$ . The procedure, using the Leibniz product rule, is to differentiate once by  $\mathbf{T}_i$  or  $\mathbf{U}_i$  and the result by each  $\mathbf{T}_j$  and  $\mathbf{U}_j$  once, with  $j$  running from 1 to  $N$ . The procedure is straightforward so only the results are presented here:

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle &= \frac{1}{\sqrt{2^{v'_i}}} \left[ \mathbf{B}_i \langle \mathbf{v}' - 1'_i | \mathbf{v}'' \rangle + \sqrt{2(v'_i - 1)} \mathbf{A}_{ii} \langle \mathbf{v}' - 2'_i | \mathbf{v}'' \rangle \right. \\ &\left. + \sum_{\substack{j=1 \\ j \neq i}}^N \sqrt{2v'_j} \mathbf{A}_{ij} \langle \mathbf{v}' - 1'_i - 1'_j | \mathbf{v}'' \rangle + \sum_{j=1}^N \sqrt{v'_j} \mathbf{E}_{ji} \langle \mathbf{v}' - 1'_i | \mathbf{v}'' - 1''_j \rangle \right] \end{aligned} \quad (24)$$

and

$$\begin{aligned} \langle \mathbf{v}' | \mathbf{v}'' \rangle &= \frac{1}{\sqrt{2^{v''_i}}} \left[ \mathbf{D}_i \langle \mathbf{v}' | \mathbf{v}'' - 1''_i \rangle + \sqrt{2(v''_i - 1)} \mathbf{C}_{ii} \langle \mathbf{v}' | \mathbf{v}'' - 2''_i \rangle \right. \\ &\left. + \sum_{\substack{j=1 \\ j \neq i}}^N \sqrt{2v''_j} \mathbf{C}_{ij} \langle \mathbf{v}' | \mathbf{v}'' - 1''_i - 1''_j \rangle + \sum_{j=1}^N \sqrt{v''_j} \mathbf{E}_{ij} \langle \mathbf{v}' - 1'_j | \mathbf{v}'' - 1''_i \rangle \right] \end{aligned} \quad (25)$$

with the first equation corresponding to an initial differentiation by  $\mathbf{T}_i$  and the second one to  $\mathbf{U}_i$ .

In the current version in GAUSSIAN, all evaluated transitions start from the vibrational ground state of the initial electronic state ( $\mathbf{T}=\mathbf{0}$ ). As a consequence, only the last recursive equation is used without the last term in the right-hand side:

$$\begin{aligned} \langle \mathbf{0}' | \mathbf{v}'' \rangle &= \frac{1}{\sqrt{2^{v''_i}}} \left[ \mathbf{D}_i \langle \mathbf{0}' | \mathbf{v}'' - 1''_i \rangle + \sqrt{2(v''_i - 1)} \mathbf{C}_{ii} \langle \mathbf{0}' | \mathbf{v}'' - 2''_i \rangle \right. \\ &\left. + \sum_{\substack{j=1 \\ j \neq i}}^N \sqrt{2v''_j} \mathbf{C}_{ij} \langle \mathbf{0}' | \mathbf{v}'' - 1''_i - 1''_j \rangle \right] \end{aligned} \quad (26)$$

### ***A priori* evaluation of the transition intensities**

Using the recursive eqs. 24 and 25, it is possible to express any overlap integral  $\langle \mathbf{v}' | \mathbf{v}'' \rangle$  with respect to  $\langle \mathbf{0}' | \mathbf{0}'' \rangle$ , which is calculated exactly. Although, there is in principle an infinite number of combinations to take into account, most of them correspond to transitions of negligible intensity.

In GAUSSIAN, an *a priori* scheme [3, 4] selects the transitions which must be taken into account. This method relies on a categorization of the latter with respect to the number of simultaneously excited modes in the final state,

called *classes*. For instance, *class 1* ( $\mathcal{C}_1$ ) represents all transitions to final vibrational states with a single excited mode  $i$ ,  $\langle \mathbf{v}' | \mathbf{0}'' + v_i'' \rangle$  and *class 0* contains the overlap integral between the vibrational ground states,  $\langle \mathbf{0}' | \mathbf{0}'' \rangle$ . Based on this division, the overlap integrals in *classes 1* and *2* are used as reference data to evaluate those to compute in each “higher” *class*, each *class* being calculated one after the other, increasing the number of excited modes in the final state. The advantages of using the overlap integrals of these *classes* are twofold. The first one is that these integrals are computationally cheap and are generated quickly even in the case of large molecules. The second interest lies in the information provided by the reference data they provide.

Depending on the approximation of the electronic transition dipole moment, FC or FCHT/HT, 2 or 3 sets of reference data are used for the prescreening. The first set  $F_{\mathcal{C}_1}$  is defined during the calculation of the transitions from *class 1* and is used for FC, FCHT and HT calculations. Its elements are defined as:

$$F_{\mathcal{C}_1}(i, v_i'') = \left| \frac{1}{\sqrt{2v_i''}} \left[ D_i \langle \mathbf{0}' | \mathbf{0}'' + v_i'' - 1_i'' \rangle + \sqrt{2(v_i'' - 1)} C_{ii} \langle \mathbf{0}' | \mathbf{0}'' + v_i'' - 2_i'' \rangle \right] \right|^2 \quad (27)$$

where the he factors  $C_{ii}$  and  $D_i$  give respectively information on the effect of the shifts in equilibrium positions and the frequencies on the overlap integrals of overtone, and more precisely on the vibrational progression of mode  $i$ .

In case of HT or FCHT calculations, a second set of data is extracted from *class 1*,  $H_{\mathcal{C}_1}$ , which stores the square of the pure Herzberg-Teller contribution for a given mode  $k$  and the corresponding transition  $\langle \mathbf{0}' | \mathbf{0}'' + v_k'' \rangle$ :

$$H_{\mathcal{C}_1}(k, v_k'') = \left| \left( \frac{\partial \mu_{if}}{\partial Q_k''} \right)_0 \sqrt{\frac{\hbar}{2\omega_k''}} \left[ \sqrt{v_k''} \langle \mathbf{0}' | \mathbf{0}'' + v_k'' - 1_k'' \rangle + \sqrt{v_k'' + 1} \langle \mathbf{0}' | \mathbf{0}'' + v_k'' + 1_k'' \rangle \right] \right|^2 \quad (28)$$

Finally, a last set  $F_{\mathcal{C}_2}$ , used for all calculations, is obtained in *class 2*, and gives information about the Duschinsky mixing of the normal modes. It contains all combinations of modes  $i$  and  $j$  but only considering the cases of an equal number of quanta for both modes ( $v_i'' = v_j''$ ):

$$F_{\mathcal{C}_2}(i, j, v_i'' = v_j'') = \left| \langle \mathbf{0}' | \mathbf{0}'' + v_i'' + v_j'' \rangle \right|^2 - F_{\mathcal{C}_1}(i, v_i'') \times F_{\mathcal{C}_1}(j, v_j'') / \left| \langle \mathbf{0}' | \mathbf{0}'' \rangle \right|^2 \quad (29)$$

From the previous description, a problem arises to define the dimensions of the arrays  $F_{\mathcal{C}_1}$ ,  $F_{\mathcal{C}_2}$  and  $H_{\mathcal{C}_1}$ , and more precisely the maximum quantum numbers  $v_{i_{\max}}''$  for *classes*  $\mathcal{C}_1$  and  $\mathcal{C}_2$ . Practically, these are set manually. Since calculations of the Franck-Condon integrals in these *classes* are computationally cheap, a relatively high limit, chosen to work in most common cases, is considered;  $\mathcal{C}_1^{\max} = 20$  for *class 1* and  $\mathcal{C}_2^{\max} = 13$  for *class 2*. These values can be set manually in the *ReadFCHT* section with the keywords `MaxC1` (or `MaxOvr`) for  $\mathcal{C}_1^{\max}$ , and the keywords `MaxC2` (or `MaxCmb`) for  $\mathcal{C}_2^{\max}$ .

The procedure to generate a vibronic spectrum is as follows. First, calculations are carried out for *class*  $\mathcal{C}_1$  and then *class*  $\mathcal{C}_2$ . For *class*  $\mathcal{C}_3$  and above, these are done in two steps. The evaluation method is initially called to set the maximum number of quanta  $v_{i_{\max}}''$  to process for each mode  $i$ . To perform this prescreening, an additional limit,  $N_I^{\max}$ , which represents the maximum number of integrals to compute in a given *class* is set. This number controls roughly the computational cost of the overall simulation, but at the risk of a loss in accuracy of the generated spectrum if it is set too low. A good compromise between resources usage and precision of the spectrum is set by default ( $N_I^{\max} = 10^8$ ). This parameter can be modified in GAUSSIAN with the keyword `MaxInt` given in the *ReadFCHT* section (see the keywords list for an explanation of the syntax).

Two thresholds,  $\epsilon_1$  and  $\epsilon_2$ , are defined for the sets of data  $F_{\mathcal{C}_1}$  and  $F_{\mathcal{C}_2}$ , respectively. In case of FCHT or HT calculations, a third threshold  $\epsilon_1^H$  for  $H_{\mathcal{C}_1}$  is also set. For each mode  $i$ , two maximum quantum numbers, respectively  $v_{i_{\max}}^{\mathcal{C}_1}$  and  $v_{i_{\max}}^{\mathcal{C}_2}$ , are obtained by decreasing the number of quanta  $v_i''$  until the conditions  $F_{\mathcal{C}_1}(i, v_i'') \geq \epsilon_1$  for the first set and  $F_{\mathcal{C}_2}(i, j, v_i'') \geq \epsilon_2$  with  $j \neq i$  for the second set, are met. For FCHT/HT calculations, a similar procedure is performed with  $H_{\mathcal{C}_1}$  and the condition  $H_{\mathcal{C}_1}(k, v_k'') \geq \epsilon_1^H$  to obtain the maximum quantum number  $v_{i_{\max}}^H$ . The highest of the maximum quantum numbers defined previously is chosen as  $v_{i_{\max}}''$ . Once the set  $\mathbf{v}_{\max}''$  has been defined, the corresponding number of integrals to calculate is roughly estimated, for a given class  $\mathcal{C}_n$ , as  $N_I = N_{\mathcal{C}_n} \times \langle \mathbf{v}_{\max}'' \rangle^n$ , where  $N_{\mathcal{C}_n}$  represents the number of combinations of the  $n$  excited oscillators and  $\langle \mathbf{v}_{\max}'' \rangle$  is the arithmetic mean of the  $N$  maximum quantum numbers. If the number of integrals to compute,  $N_I$  is higher than the allowed limit  $N_I^{\max}$ , the thresholds  $\epsilon_1$  and  $\epsilon_2$  (and  $\epsilon_1^H$  for FCHT and HT calculations) are increased and the set of maximum quantum numbers  $\mathbf{v}_{\max}''$  is re-estimated. When the condition  $N_I \leq N_I^{\max}$  is fulfilled, all transition dipole moment integrals are computed up to the chosen maximum number of quanta  $v_{i_{\max}}''$  for each mode.



## Evaluating the reliability of the prescreening with the sum rules

To check the reliability of the prescreening method, the total intensity calculated after each *class* is checked with the total intensity expected using analytic sum rules. The sum of all transition intensities is given by,

$$I^{\text{tot}} = \sum_{'} \rho' \sum_{''} |\langle \Psi' | \boldsymbol{\mu} | \Psi'' \rangle|^2 \approx \sum_{'} \rho' \sum_{''} |\langle \mathbf{v}' | \boldsymbol{\mu}_{if} | \mathbf{v}'' \rangle|^2 \quad (30)$$

where the first sum symbol represents the summation over all possible vibrational initial states and the second one the ensemble of all final states.  $\rho'$  is the Boltzmann population of each initial state.

Expanding the square in the previous equation and accounting for the orthonormality of the vibrational wave functions, the intensity  $I^{\text{tot}}$  can be written:

$$I^{\text{tot}} = \sum_{'} \rho' \langle \mathbf{v}' | \boldsymbol{\mu}_{if} \cdot \boldsymbol{\mu}_{if} | \mathbf{v}' \rangle \quad (31)$$

In case of FC calculations, where  $\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}(\mathbf{Q}_0'')$ , eq. 31 can be written:

$$I^{\text{tot}} = |\boldsymbol{\mu}_{if}(\mathbf{Q}_0'')|^2 \sum_{'} \rho' \langle \mathbf{v}' | \mathbf{v}' \rangle = |\boldsymbol{\mu}_{if}(\mathbf{Q}_0'')|^2 \quad (32)$$

In the framework of the Herzberg-Teller approximation of the electronic transition dipole moment (FCHT and HT calculations), the computation of  $I^{\text{tot}}$  is more involved. Considering the Taylor expansion of the electronic transition dipole moment given in eq. 5, and eq. 31, it is straightforward to see that annihilation and creation operators will be needed to obtain the sum rules. However, the development of  $\boldsymbol{\mu}_{if}$  in the Taylor series about the equilibrium geometry of the final state is not immediate because the annihilation and creation operators obtained this way act on the quantum states of the final state and not on the initial state, with respect to our previous definition in eq. 5. A simple solution would be to develop  $\boldsymbol{\mu}_{if}$  in a Taylor series about the equilibrium geometry of the initial state. However, while the equality  $\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}(\mathbf{Q}') = \boldsymbol{\mu}_{if}(\mathbf{Q}'')$  is true, this is generally not the case when considering the Taylor series around each equilibrium geometry. As a consequence, two analytic limits are defined depending on the state of reference,  $I_{\mathbf{Q}'}^{\text{tot}}$  for the initial state and  $I_{\mathbf{Q}''}^{\text{tot}}$  for the final state.

The first analytic limit,  $I_{\mathbf{Q}'}^{\text{tot}}$  is rather straightforward to evaluate:

$$I_{\mathbf{Q}'}^{\text{tot}} = \sum_{'} \rho' \langle \mathbf{v}' | |\boldsymbol{\mu}_{if}(\mathbf{Q}_0')|^2 + \sum_{k=1}^N \left| \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q'_k} \right)_0 \right|^2 Q_k'^2 | \mathbf{v}' \rangle \quad (33)$$

Using the annihilation and creation operators, the analytic limit is given by the formula,

$$I_{\mathbf{Q}'}^{\text{tot}} = |\boldsymbol{\mu}_{if}(\mathbf{Q}_0')|^2 + \sum_{'} \rho' \sum_{k=1}^N \left| \left( \frac{\partial \boldsymbol{\mu}_{if}(\tau)}{\partial Q'_k} \right)_0 \right|^2 \frac{\hbar}{2\omega'_k} (2v'_k + 1) \quad (34)$$

In the case of  $I_{\mathbf{Q}''}^{\text{tot}}$ , additional steps are needed to evaluate the analytic limit:

$$I_{\mathbf{Q}''}^{\text{tot}} = \sum_{'} \rho' \langle \mathbf{v}' | |\boldsymbol{\mu}_{if}(\mathbf{Q}_0'')|^2 + \sum_{k=1}^N \left| \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q''_k} \right)_0 \right|^2 Q_k''^2 | \mathbf{v}' \rangle \quad (35)$$

$$= \sum_{'} \rho' \langle \mathbf{v}' | \left| \boldsymbol{\mu}_{if}(\mathbf{Q}_0'') + \sum_{k=1}^N \left( \frac{\partial \boldsymbol{\mu}_{if}}{\partial Q''_k} \right)_0 \sum_{l=1}^N (J^T)_{kl} Q'_l + (J^T)_{kl} K_l \right|^2 | \mathbf{v}' \rangle \quad (36)$$

where the inverse of the Duschinsky transformation given in eq. 14 has been used to express  $\mathbf{Q}''$  with respect to  $\mathbf{Q}'$ .

After using the operators of the second quantization,  $I_{\mathbf{Q}''}^{\text{tot}}$  is given by the relation:

$$\begin{aligned}
I_{\mathbf{Q}''}^{\text{tot}} = & |\boldsymbol{\mu}_{if}(\mathbf{Q}_0'')|^2 + \sum_{\tau=x,y,z} \sum_{l=1}^N \rho' \left[ \right. \\
& \left. \left\{ \sum_{k=1}^N \left( \frac{\partial \mu_{if}(\tau)}{\partial Q_k''} \right)_0 \sum_{l=1}^N (J^T)_{kl} \sum_{m=1}^N \left( \frac{\partial \mu_{if}(\tau)}{\partial Q_m''} \right)_0 (J^T)_{ml} \frac{\hbar}{2\omega_l'} (2v_l' + 1) \right\} \right. \\
& \left. \left\{ -2\mu_{if}(\mathbf{Q}_0'', \tau) \sum_{k=1}^N \left( \frac{\partial \mu_{if}(\tau)}{\partial Q_k''} \right)_0 \sum_{l=1}^N (J^T)_{kl} K_l \right\} \right. \\
& \left. \left\{ + \sum_{k=1}^N \left( \frac{\partial \mu_{if}(\tau)}{\partial Q_k''} \right)_0 \sum_{l=1}^N (J^T)_{kl} K_l \sum_{m=1}^N \left( \frac{\partial \mu_{if}(\tau)}{\partial Q_m''} \right)_0 \sum_{n=1}^N (J^T)_{mn} K_n \sum_{l=1}^N \right\} \right]
\end{aligned} \tag{37}$$

where the summation over the Cartesian coordinates  $(x, y, z)$  is explicitly given.

The choice of  $I_{\mathbf{Q}'}^{\text{tot}}$  or  $I_{\mathbf{Q}''}^{\text{tot}}$  in GAUSSIAN depends on the available data. In the case of absorption, the excited state is  $\mathbf{Q}''$ , so  $\boldsymbol{\mu}_{if}(\mathbf{Q}_0'')$  and  $\partial \boldsymbol{\mu}_{if} / \partial \mathbf{Q}''$  are known. Hence, the analytic sum chosen as a reference to evaluate the convergence of the spectrum is  $I_{\mathbf{Q}''}^{\text{tot}}$ . In case of emission, the reference is  $I_{\mathbf{Q}'}^{\text{tot}}$ .

The chosen analytic limit,  $I^a$  ( $I^{\text{tot}}$  for FC calculations,  $I_{\mathbf{Q}'}^{\text{tot}}$  or  $I_{\mathbf{Q}''}^{\text{tot}}$  for FCHT/HT calculations) is used to calculate the spectrum convergence (called in the GAUSSIAN output the spectrum progression) with the following relation:

$$\text{spectrum progression} = \frac{\sum_{l'} \rho' \sum_{l''} |\langle \mathbf{v}' | \boldsymbol{\mu}_{if} | \mathbf{v}'' \rangle|^2}{I^a} \tag{38}$$

In the current implementation of GAUSSIAN, the temperature is not yet taken into account, so the relation used in practice is:

$$\text{spectrum progression} = \frac{|\langle \mathbf{0}' | \boldsymbol{\mu}_{if} | \mathbf{v}'' \rangle|^2}{I^a} \tag{39}$$

### 3 Quick start

In its most concise form, the generation of a vibrationally-resolved electronic spectrum in GAUSSIAN requires a single keyword representing the terms of the Taylor series given in eq. 5 that must be taken into account.

- FC: zeroth-order term of the Taylor series  $[\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}(\mathbf{Q}_0'')]$ , suitable for fully-allowed transitions
- FCHT: zeroth- and first-order terms of the Taylor series  $[\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}(\mathbf{Q}_0'') + \sum_{k=1}^N (\partial \boldsymbol{\mu}_{if} / \partial Q_k'') Q_k'']$ , suitable for most cases spanning from fully-allowed to dipole-forbidden transitions
- HT: first-order term of the Taylor series  $[\boldsymbol{\mu}_{if} = \sum_{k=1}^N (\partial \boldsymbol{\mu}_{if} / \partial Q_k'') Q_k'']$ , suitable for dipole-forbidden transitions or to show the contribution of the Herzberg-Teller approximation to the spectrum.

Additionally, GAUSSIAN will need the checkpoint file containing the data of the final state. This file must be given after the standard input (in general, below the *molecule specification*), the data for the initial state being taken from the current calculation.

Two methods can be distinguished to generate the vibrationally-resolved electronic spectra. The first one is to simulate the latter as soon as the frequencies of the initial state have been calculated. In this case, two GAUSSIAN jobs are required, assuming the structures of the initial and final states are already optimized:

1. Calculation of the frequencies for the final state
2. Calculation of the frequencies for the initial state followed by the generation of the spectrum.

In the input file for the second step, the keywords FC, FCHT, HT is given in `Frequency` as follows (the example below is limited to the case of the Franck-Condon approximation):

*Link 0 Commands*

*Route section (# lines) with* `Frequency=(FC, SaveNM) NoSymm`

*Title section*

*Molecule specification*

*Name of the checkpoint file generated in step 1*

In the example above, two additional keywords are used. While not mandatory, `SaveNM` will make GAUSSIAN save the frequencies and normal modes in the checkpoint file. This option is necessary to deal with QM/MM calculations or when dealing with frozen atoms to extract correctly the normal modes and frequencies. As a consequence, it is advisable to use it every time when computing the frequencies for both states and avoid possible issues caused by the impossibility of GAUSSIAN to recompute correctly the eigenvalues and eigenvectors of the Hessian matrix.

Since this method requires the computation of frequencies each time a spectrum must be generated, it is not well suited when diverse parameters must be tried for the generation of the spectrum. A second way of using GAUSSIAN is through a 3-steps procedure where the last step of the previous method is broken down in two separate steps, first the calculation of the frequencies and then the generation of the spectrum. Schematically, this gives the following procedure:

1. Calculation of the frequencies for the initial state
2. Calculation of the frequencies for the final state
3. Generation of the electronic spectra

The order in which the first two steps are performed is not important and they can be done simultaneously. We will however consider this sequence is respected in the following description

While this method seems more complex, it is also more flexible as GAUSSIAN works as a stand-alone program dedicated to the simulation of the electronic spectra. The input files for the first two steps are classical ones to compute frequencies with the keyword `SaveNM` used in `Frequency`. The input file for the last step is as follows:

*Link 0 Commands*

`%Chk=`*Name of the checkpoint file generated in step 2*

`#P` `Geom=AllCheck` `Frequency=(ReadFC, FC, SaveNM) NoSymm`

*Name of the checkpoint file generated in step 1*

The options `Geometry=AllCheck` and `Frequency=ReadFC` are described in the GAUSSIAN manual. Basically, they let us extract all necessary data from the checkpoint file given in the line starting by `%Chk=` without the need to perform long calculations before the procedure to generate the spectrum is called.

As mentioned before, this approach is particularly interesting when investigating the best settings to generate an accurate electronic spectrum, using the parameters described in the section below.

## Description of the output

Whatever the chosen procedure, the output will be similar and structured as follows. The block in the output related to the generation of the spectrum starts with the following output:

```
*****  
Generation of the Franck-Condon spectrum  
*****
```

General information is then given on the type of calculation, the approximation of the electronic transition dipole moment and the type of transition:

```
Approx. of the electronic transition dipole moment: FC  
Type of transition requested: ONE-PHOTON ABSORPTION
```

The output presented above is an example showing the case of an absorption spectrum with the electronic transition dipole moment considered as constant during the transition.

GAUSSIAN then describes the procedure of extraction of the data from the sources. In the case of our quick start procedure, the output will be:

```
Data for initial state taken from current calculation.  
Passed-in normal modes used.  
  
Data for final state taken from checkpoint file "checkpoint file of step 1"  
Normal modes recovered from file.  
  
Initial state structure is set in Eckart orientation.  
Final state structure is superposed to it.
```

The last line is followed by the geometry of the system in both states after reorientation. As explained in the description of the Franck-Condon principle, the calculation of the vibronic spectra requires the minimization of nuclear displacements during the transition. Although rigorous separation between rotations and vibrations is, of course, not possible, their coupling for the initial electronic state can be minimized by putting the molecule in the Eckart orientation (origin in the mass center and Cartesian axes along the principal inertia moments) using the standard GAUSSIAN orientation for the ordering of Cartesian axes. Two options are next possible for the final electronic state, namely to use its own Eckart orientation, or to minimize the angular momentum between initial and final structures. The second one is the default because it minimizes the contribution of rotations to the shift vector and the Duschinski matrix.

Next, the molecule in the final electronic state is firstly rotated using the same rotation matrix of the reference state and next a new rotation matrix is computed in order to minimize the angular momentum between initial and final structure

$$\sum_{i=1}^{N_A} M_{ii} (\mathbf{X}'_i \wedge \mathbf{X}''_i) \quad (40)$$

where  $\mathbf{M}$  is the diagonal matrix of the atomic masses,  $\mathbf{X}'_i$  and  $\mathbf{X}''_i$  are the triplets of Cartesian coordinates for the nucleus  $i$  in the initial and final states, respectively.

This two step procedure [10] allows to avoid numerical problems when the geometries and/or starting orientations of initial and final states are strongly different. There are two options to build the rotation matrix, using Euler angles [11–13] or quaternions [14, 15], respectively. Although the latter approach (which is the default) should be more stable and direct, there are cases in which it fails, so that, after a predetermined number of iterations, the program shifts to Euler angles.

The actual calculation is then presented:

```
-----  
Overlap integrals computation  
-----
```

```
Energy of the 0-0 transition: Calculated value cm-1
```

```
Notes about the overlap integrals description:
```

- DeltaE is the relative energy of the transition (wrt 0-0)
- TDMI<sup>2</sup> is the square of the transition dipole moment integral
- Intensity is the line intensity (absolute value)

A list of the most intense transitions is then printed. They are listed by incrementing *class*. The general format is:

```
Initial State: <0|  
Final State: |X^X, X^X>  
DeltaE =      X.XXXX | TDMI^2 = X.XXXXEXXX, Intensity = X.XXXXEXXX  
.....
```

The first line represents the initial state and the second line the final state. The third line contains the energy of the transition with respect to the energy of the transition between the vibrational ground state,  $\langle \mathbf{0}' | \mathbf{0}'' \rangle$ , the value  $|\langle \mathbf{v}' | \boldsymbol{\mu}_{if} | \mathbf{v}'' \rangle|^2$ , and the intensity of the corresponding spectrum line. The character *x* given above represents a digit or a sign.

Once a *class* has been treated, the convergence of the spectrum is printed:

```
++ Spectrum progression:  XX.XX%
```

Finally, the spectrum generated by GAUSSIAN is printed:

```
+-----+  
| Final Spectrum |  
+-----+  
  
Axis X = Energy (in cm-1)  
Axis Y = Intensity (in arbitrary units)  
  
-----  
XXXXX.XXXX      X.XXXXXXDXXX
```

## 4 List of options

While the default behavior of GAUSSIAN is set to give satisfactory results in most cases, it can be not well suited for particular cases or poorly adapted to specific requirements from the user. A number of options exist to extensively parameterize the calculations and provide a satisfactory analysis of the case of interest. These options need to be given in a specific section referred to as the “*ReadFCHT section*”. This section lies below the standard GAUSSIAN input and is activated by adding the keyword “ReadFCHT” in the option Frequency. The resulting GAUSSIAN input is structured as follows:

|  |
|--|
| <i>Link 0 Commands</i>   |
| <i>Route section (# lines) with</i> Frequency= (ReadFCHT)            |
| <i>Title section</i>   |
| <i>Molecule specification</i>  |
| <i>Optional additional sections used by links called before I716</i> |
| <i>ReadFCHT section</i>  |

The description of the different sections above the *ReadFCHT section* can be found in the GAUSSIAN 09 manual and is outside the scope of this document. The options available for the simulation of vibronic spectra using the Franck-Condon principle are listed in the table below, organized by functions. To make the reading of the latter easier, the lines are differentiated by alternating backgrounds of different colors. Following this scheme, two keywords in the same “line” are equivalent (ex: ABS and ABSORPTION). Additionally, blocks are defined between two consecutive horizontal black lines. All keywords given in the same block of lines correspond to the same option and are mutually exclusive (ex: FC, FCHT and HT). In general, when several keywords related to the same option are given, only the last one is taken into account and the others are discarded.

*Note:* Regarding the last group of options dealing with forced calculations, it is highly advisable to avoid their use by default as they will bypass protections of GAUSSIAN regarding the soundness of the calculations. As a consequence, they should be used carefully.

| Keyword                                       | Values      | Description   |
|---|-------------|---|
| <b>General parameters of the calculations</b> |             |   |
| <b>FC</b>                                     | <i>None</i> | <b>(Default)</b> The electronic dipole moment is assumed constant during the transition. This approximation is generally well suited for fully-allowed transition.  |
| FCHT  | <i>None</i> | The electronic transition dipole moment is developed in a Taylor series about the equilibrium geometry of the final state up to the first-order term included. This approximation is more general than FC and works on diverse cases, from fully-allowed to dipole-forbidden transitions. |
| HT  | <i>None</i> | Only the linear variation of the electronic transition dipole moment with the normal coordinates of the final state is taken into account (first-order term of the Taylor series given in eq. 5).   |
| <b>ABSORPTION</b><br><b>ABS</b>               | <i>None</i> | <b>(Default)</b> The simulated vibronic spectrum corresponds to a one-photon absorption transition.   |
| EMISSION<br>EMI                               | <i>None</i> | The simulated vibronic spectrum corresponds to a one-photon emission transition.  |
| <b>Sources of input data</b>                  |             |   |
| <b>CALC1</b>                                  | <i>None</i> | <b>(Default)</b> Data for the initial state are taken from the current GAUSSIAN job.  |
| CHK1  | <i>None</i> | Data for the initial state are taken from the checkpoint file provided below the <i>ReadFCHT section</i> .  |
| OUT1  | <i>None</i> | Data for the initial state are taken from the GAUSSIAN output file provided below the <i>ReadFCHT section</i> .   |
| CALC2   | <i>None</i> | Data for the final state are taken from the current GAUSSIAN job.   |

| Keyword     | Values      | Description  |
|-------------|-------------|--|
| <b>CHK2</b> | <i>None</i> | <b>(Default)</b> Data for the final state are taken from the checkpoint file provided below the <i>ReadFCHT</i> section.             |
| OUT2        | <i>None</i> | Data for the final state are taken from the GAUSSIAN output file provided below the <i>ReadFCHT</i> section.                         |
| NSTATE      | 1           | Chooses the electronic state from which the data relative to the electronic transition dipole moments and the derivatives are taken. |

#### User-given input data or modification options

|               |                     |  |
|---------------|---------------------|--|
| InpDEner      | 0.0 (= <b>Off</b> ) | Replaces the calculated difference of energy between both electronic states involved in the transition by the value given by the user. Such value is expected in Hartree and is not taken in account if null.  |
| SclVec        | <i>None</i>         | A mode-specific scaling algorithm based on the Duschinsky matrix is used to compute new frequencies for the final state using the differences between the calculated frequencies for the initial states and user-given ones listed below the <i>ReadFCHT</i> section. The frequencies are expected in $\text{cm}^{-1}$ . See ref. [16] for more details on its behavior. |
| <b>JDusch</b> | <i>None</i>         | <b>(Default)</b> Uses the correct Duschinsky matrix to perform the calculations.   |
| JIdent        | <i>None</i>         | Uses an identity matrix instead of the Duschinsky matrix. In this case the mode-mixing is ignored.   |

#### Parameterization of the GAUSSIAN output

|            |                   |   |
|------------|-------------------|---|
| PRTMAT     | 0 (= <b>Off</b> ) | <p>Prints the Sharp and Rosenstock matrices or the Duschinsky matrices and vectors. A digit is assigned to each matrix as follows:</p> <ol style="list-style-type: none"> <li>1. Duschinsky matrix <b>J</b>. Please note that, with respect to eq. 14, <math>\mathbf{J}^T</math> is printed.</li> <li>2. shift vector <b>K</b></li> <li>3. Sharp and Rosenstock matrix <b>A</b></li> <li>4. Sharp and Rosenstock vector <b>B</b></li> <li>5. Sharp and Rosenstock matrix <b>C</b></li> <li>6. Sharp and Rosenstock vector <b>D</b></li> <li>7. Sharp and Rosenstock matrix <b>E</b></li> </ol> <p>The digits corresponding to the matrices to be printed are placed side by side to form a number that is given as the value of PRTMAT. Ex: PRTMAT=12 corresponds to printing the Duschinsky matrix and shift vector.</p> |
| ALLSPECTRA | <i>None</i>       | Prints the spectra corresponding to each <i>class</i> in addition to the final, total spectrum.   |
| PRTINT     | 0.01              | Prints data (assignment, energy, intensity) of the transitions which have an intensity ( $ \langle \mathbf{v}'   \boldsymbol{\mu}_{if}   \mathbf{v}'' \rangle ^2$ ) above or equal to 1% of the total analytic limit.   |

#### Setting of the spectrum layout

| Keyword  | Values      | Description  |
|----------|-------------|--|
| SPECMIN  | -1000.0     | Sets (in $\text{cm}^{-1}$ ) the lower bound of the spectrum. The value is normally given relative to the energy of the transition between both vibrational ground states.  |
| SPECMAX  | +8000.0     | Sets (in $\text{cm}^{-1}$ ) the upper bound of the spectrum. The value is normally given relative to the energy of the transition between both vibrational ground states.  |
| NORELIO0 | <i>None</i> | Using this keyword, GAUSSIAN expects the lower and upper bound of the spectrum to be given in absolute values (not relative to the 0-0 transition). This keyword should be used together with both SPECMIN and SPECMAX to avoid an unexpected behavior.                              |
| SPECRES  | 8.0         | Resolution of the spectrum given by the difference of energy between two contiguous measuring points (in $\text{cm}^{-1}$ ). It is noteworthy that a very high resolution (given by a small value of SPECRES) can greatly hamper the computational speed of the spectrum generation. |
| SPECHWHM | 135.0       | Sets the Half-Width at Half-Maximum (in $\text{cm}^{-1}$ ) for the convolution of the spectrum using a Gaussian distribution. A large value of SPECHWHM coupled to a small value of SPECRES can cause a steep increase of the computational times.                                   |

#### Modification of the behavior of the *a priori* scheme to chose the most relevant transition

|                 |             |  |
|-----------------|-------------|--|
| MAXOVR<br>MAXC1 | 20          | Sets the maximum quantum number that has to be considered for each mode of $\mathcal{C}_1$ ( $\mathcal{C}_1^{\text{max}}$ ).   |
| MAXCMB<br>MAXC2 | 13          | Sets the maximum quantum number to consider for each mode involved in the combination bands in $\mathcal{C}_2$ ( $\mathcal{C}_2^{\text{max}}$ ).   |
| MAXINT          | 100         | Sets the maximum number of integrals ( $N_I^{\text{max}}$ , expressed in million) to compute for each <i>class</i> above $\mathcal{C}_2$ .   |
| NOINTAN         | <i>None</i> | Deactivates the usage of analytic formulae to compute the overlap integrals in <i>classes</i> $\mathcal{C}_1$ and $\mathcal{C}_2$ . By default, analytic formulae are used when available for these <i>classes</i> . |

#### Termination criteria for the spectrum generation

|          |     |   |
|----------|-----|---|
| MAXBANDS | 7   | Sets the maximum <i>class</i> to consider. Calculations can end before if there are not enough excited modes or DELTASP is also defined and the condition imposed by the latter is met before.                        |
| DELTASP  | 0.0 | Sets a condition on the spectrum convergence. If the spectrum progression with respect to the total intensity between two consecutive <i>classes</i> is below DELTASP (in absolute value), then the calculations end. |

#### Forcing calculations<sup>4</sup>

|                  |             |  |
|------------------|-------------|--|
| ForceFCCalc      | <i>None</i> | Forces the calculation of the Franck-Condon integrals even if the overlap integral between the vibrational ground states of the initial and final states is very low ( $ \langle \mathbf{0}'   \mathbf{0}'' \rangle ^2 < 10^{-4}$ ). |
| ForcePrtSpectrum | <i>None</i> | Forces the printing of the final spectrum even if the total progression is low (below 50%).  |

The structure of the GAUSSIAN input file starting from the *ReadFCHT* section is as follows, each optional block of data (“*SciVec*” and “*Sources*”) being terminated by a blank line:

<sup>4</sup>*Warning:* The keywords describe in this section should be used with care as they might lead to results whose reliability is unpredictable



*ReadFCHT section*

*[blank line]*

*User-given frequencies for the initial state (necessary for Sc1Vec)*

*[blank line]*

*Name of the file containing the data for the initial state (if different from the current GAUSSIAN job)*

*Name of the file containing the data for the final state (if different from the current GAUSSIAN job)*

*[blank line]*

“Sc1Vec” block

“Sources” block

By default, only the name of the checkpoint file containing the data of the final state needs to be given after the *ReadFCHT section*.

## 5 Some practical examples

The examples described here are taken from reference [17] and shows the parameters used in the *ReadFCHT section* to carry out the calculations. The GAUSSIAN inputs presented here are based on the 3-steps usage of GAUSSIAN, where the last step is dedicated to the generation of the spectrum.

### Photodetachment spectrum of $SF_6^-$ : parameterizing the prescreening method

In the photodetachment spectrum of  $SF_6^-$ , a significant elongation of the S-F bond upon electron attachment is found. As a consequence, the potential curves of the normal mode corresponding to the S-F symmetric stretching are noticeably displaced (see Fig. 2 in ref [18]). When generating the photodetachment spectrum of  $SF_6^-$  with the standard parameter, an insufficient value of MAXC1 is set and only a partial spectrum is obtained. As a consequence, the following input file is used for the generation of the complete spectrum:

```
%Chk=SF6_neutral_freq.chk
#P  Geom=AllCheck  Freq=(ReadFC,FC,SaveNM,ReadFCHT)  NoSymm

  PRTMAT=12  MAXC1=100  MAXBANDS=4  SPECHWHM=0.5

SF6_anion_freq.chk
```

$C_1^{\max}$  is set to a safe, high value since the cost of the prescreening is cheap. When performing the calculation, GAUSSIAN will find that it does not need to go up to *class 7* and will safely stop the calculations. Here, we set manually the correct limit.

### $S_1 \leftarrow S_0$ absorption spectrum of Anisole: parameterizing the spectrum layout

To compare the theoretical spectrum obtained with GAUSSIAN and the experimental REMPI spectrum, it is necessary to modify the default values of the parameters corresponding to the spectrum layout. This is done with the following input

```
%Chk=anisole_S0.chk
#P  Geom=AllCheck  Freq=(ReadFC,FC,SaveNM,ReadFCHT)  NoSymm

  PRTMAT=12  NORELI00  SPECMIN=37900  SPECMAX=42000  SPECHWHM=1.  SPECRES=1.

anisole_S1.chk
```

The absolute values of the spectrum bounds are given here and a very fine spectrum is requested.

Although the spectrum layout obtained this way is very similar to the experimental one, an energy shift was observed for several peaks, with the frequencies calculated at the harmonic level. To correct this, anharmonic frequencies had to be used. However, they could not be straightforwardly obtained for the final, excited state with the time-dependent density functional theory (TD-DFT) computations. Hence, the mode-specific scaling scheme [16] implemented in GAUSSIAN and available with the keyword `ScIVec` was used. The anharmonic frequencies calculated for the ground state [19] were used as input as follows:

```
%Chk=anisole_S0.chk
#P Geom=AllCheck Freq=(ReadFC,FC,SaveNM,ReadFCHT) NoSymm

PRTMAT=12 NORELI00 SPECMIN=37900 SPECMAX=42000 SPECHWHM=1. SPECRES=1.
ScIVec

  86.39  200.38  252.59  257.52  417.46  437.57  510.86  554.26  623.74
 696.93  757.21  784.32  811.61  883.10  958.95  981.60  994.62 1018.63
1040.32 1082.75 1146.70 1164.42 1177.75 1177.40 1238.75 1305.54 1336.45
1467.80 1454.61 1479.55 1465.73 1494.69 1582.76 1601.40 2869.62 2902.51
2993.57 3006.94 3042.47 3047.04 3068.53 3077.61

anisole_S1.chk
```

GAUSSIAN then corrects the harmonic frequencies of the excited state with a mode-specific scaling to account for the anharmonicity. Using the harmonic frequencies present in the checkpoint ( $\omega'_{\text{harm}}$ ) and the user-given data ( $\omega'_{\text{anh}}$ ), a scaling vector  $\alpha'$  is calculated:

$$\alpha'_i = \omega'_{\text{anh}} / \omega'_{\text{harm}}$$

Using the square elements of the Duschinsky matrix, the scaling vector for the excited state  $\alpha''$  is deduced from  $\alpha'$  with the relation,

$$\alpha''_j = \sum_{i=1}^N J_{ij}^2 \alpha'_i$$

The new anharmonic frequencies  $\omega''_{\text{anh}}$  are then calculated as:

$$\omega''_{\text{anh}} = \alpha''_i \omega''_{\text{harm}}$$

GAUSSIAN prints in output the scaling vectors  $\alpha'$  and  $\alpha''$  as well as the frequencies that will be used in each state for the calculation of the vibronic spectrum.

## 6 Description of the errors reported by GAUSSIAN

Several controls are performed in GAUSSIAN to check the validity of the calculations. Depending on the origin of the problem found, calculations can be aborted with an error or a simple warning can be issued. While the former will result in a termination of the calculations, the latter are there to draw the attention of the user on potential issues. In this section, we present a brief overview of the most common error and warning messages, their origin as well as possible workarounds or leads that should be investigated to solve them.

### Errors

#### - Cannot extract data for both states from the current calculations

This error is due to the fact that GAUSSIAN attempts to extract all data from the current job.

It is likely that CALC1 has been given without setting the source of data for the final state. By default, GAUSSIAN will have set the current calculation for the final state.

- **WARNING: Charge (or Multiplicity) is different between initial and final states. Calc. cannot be done out with the trans. dip. mom. in the data files**

This error is raised if a FCHT or HT calculation is requested and GAUSSIAN cannot use the transition electronic dipole moment and its derivatives that were found in the source files.

For this kind of calculation, the transition is generally fully-allowed and the FC approximation should be sufficient.

- **ERROR: The Franck-Condon factor corresponding to the overlap integral between both vibrational ground states is too small:**  $|\langle 0' | 0 \rangle|^2 = x$

This error indicates that it is very likely that the underlying theory used to generate the spectrum, the Franck-Condon principle, is unsuitable for the case of interest. This is a typical issue when the equilibrium geometry of the initial and final states are noticeably different. This can happen when one of the structures is planar in one electronic state and not planar in the other electronic state.

Another indicator of this problem is the Duschinsky matrix (which can be displayed with the option "PRTMAT=1" in the *ReadFCHT section*) that shows the projection of the normal modes of one state on those of the other state. In this case, the Duschinsky matrix is rather diffuse, that is to say that many normal coordinates of the final state are expressed by a combination of a rather large number of normal modes of the initial state.

If the calculations must be carried anyway, this error can be bypassed with the keyword `ForcedFCCalc`. **However**, please note that the resulting spectrum will be likely unreliable and the corresponding calculations should be considered as tests.

- **ERROR: The final spectrum progression is too low and the resulting spectrum may be unreliable. To print the spectrum nevertheless, please use the keyword FORCEPRTSPECTRUM.**

This error is often related to the same reasons as the previous one, that is to say that the Franck-Condon principle can be unsuitable to the case of interest.

If this it is not the case, the problem may be caused by too low number of calculated transitions. Several options may resolve this problem. The first one is to increase MAXBANDS which correspond to the highest class to be treated. If it has been set very low, then the spectrum convergence will be limited. Other possibility is that the values of MAXC1/MAXOVR and/or MAXC2/MAXCBI are set too low. If this is the case, warnings should have been issued during the calculations:

**Warning: insufficient num. of quanta for mode  $i$ ,**

Finally, this error can also be caused by a low number of transitions to compute in each *class* (MAXINT).

## Warnings

- **WARNING: Value for PRTINT is too low. Reset to 1.0D-6. Be careful that it can cause a very verbose output of Gaussian.**

Setting a very low value of PRTINT might cause the generation of a very large output file. PRTINT is given as a fraction of the total analytic sum. As a consequence, setting PRTINT=1.D-3 for example will print the assignment of all integrals which contribute to at least 0.1% to the total intensity.

- **Warning: insufficient num. of quanta for mode  $i$ ,**

GAUSSIAN found that the condition  $F_{C_1}(i, C_1^{\max}) \geq \epsilon_1$  was true for the normal mode  $i$ . Such a condition means that the parameter MAXC1 must be set with a higher value than the current one (by default, MAXC1=20).

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