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Accurate calculations of second-order vibronic reduction factors for C_{60} ions

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Abstract

An effective Hamiltonian containing Jahn–Teller (JT) first- and second-order vibronic reduction factors (RFs) is a convenient way of modelling the spectroscopic properties of solids and molecules in which vibronic interactions are important. It can act as a bridge between experimental data and basic theory. In particular, second-order RFs can give valuable information on many of the fundamental properties of strongly coupled systems. As interest in the icosahedral fullerene molecules and ions has grown over the last few years, it has become necessary to be able to calculate values for second-order RFs in icosahedral symmetry in terms of more fundamental vibronic coupling parameters. Following on from earlier work on the icosahedral $T \otimes h$ JT system, we present here results of such calculations of the second-order vibronic RFs for the icosahedral $G \otimes g$, $G \otimes h$, $H \otimes g$ and $H \otimes h$ JT systems. These systems are relevant for the ground and excited states of C_{60} anions and cations. The calculations are based on the Franck–Condon approximation followed by additional non-Condon corrections. Previous work has demonstrated that such an approach can give values for the RFs close to those deduced from experiments.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

The electronic properties of individual fullerene ions are often much influenced by the vibrations of the fullerene molecule, due to the Jahn–Teller (JT) coupling [1, 2] between the electrons and the nuclear cage. This is particularly true when the electrons are in a degenerate orbital state [3]. Icosahedral symmetry gives rise to orbital triplet (T_1, T_2), quadruplet (G) and quintuplet (H) states (in additional to singlet A states). This means that the ground and/or the excited states of fullerene molecules and ions can be subject to various different JT effects. There are many ways in which the JT coupling can influence the data obtained during an experimental investigation and it is important to find out the nature of the physical principles involved in these influences.

A very convenient description of the properties of the various JT systems can be obtained using an effective Hamiltonian which provides a bridge between theory and the experimental data. In particular, it is used to describe the effects of electronic perturbations through the introduction of so-called vibronic reduction factors (RFs) [4]. RFs are convenient parameters as they involve directly both the frequencies of the vibrations and the strength of the JT coupling. Their measurement by experiment and their theoretical evaluation based on a suitable model can then be compared. The most simple are the first-order RFs (foRFs) derived from first-order perturbation theory, as they are relatively easy to calculate and can be measured directly from an analysis of experimental data.

Many JT systems contain minima (or wells) in the ground adiabatic potential energy surface (APES). foRFs can then quench the effect of many perturbations drastically. This is because the overlap integral between vibrational states localized in individual potential wells located in the APES may be very small. Typically, foRFs decrease exponentially from unity to zero as the vibronic coupling strength increases. For example, this quenching drastically reduces the effects of spin–orbit coupling in many cubic systems. In contrast, however, second-order RFs (soRFs) do not generally involve this overlap integral and they consequently remain important at strong coupling strengths. They can therefore dominate the effects of the foRFs, as is true in the case of spin–orbit coupling. Another property of soRFs is that they can introduce additional terms into the effective Hamiltonian. The major problem is that soRFs are generally difficult to calculate with high accuracy, except in the limit of infinitely strong coupling when the Franck–Condon (FC) approximation [5] is valid. However, in order to overcome many of these difficulties, a new procedure has been devised involving non-Condon corrections to the standard FC method [6]. This extends the range of applicability of the results to much lower coupling strengths. The validity of the theory has been successfully tested against the well known case of the cubic $T \otimes t_2$ JT system. It was then used to calculate the soRFs in the icosahedral $T \otimes h$ JT system, which is relevant to the ground state of the C_{60}^{-} anion.

The overall aim of the work described here is to provide a comprehensive and systematic account of the basic theory of soRFs which arise in the remaining icosahedral systems, which will be applicable to higher charge states C_{60}^{n-} of fullerene anions. We will give the most important results obtained for the $G \otimes g$, $G \otimes h$, $H \otimes g$ and $H \otimes h$ JT systems. Although not explicitly given, this provides information also on the combined JT systems $G \otimes (g \oplus h)$ and $H \otimes (g \oplus h)$. Section 2 summarizes the underlying principles involved in using the FC and non-Condon corrections to calculate the soRFs. Formulae defining the soRFs are also given and explained in physical terms. Sections 3 and 4 summarize the basic formulae and definitions of the RFs including the non-Condon corrections. Sections 5 and 6 give a selection of results of calculations of the soRFs for the G and H orbital states respectively. Finally, the results and their relevance in the modelling processes are discussed in section 7 together with concluding remarks.

2. The physical principles of the Franck–Condon approximation and the non-Condon correction

The general vibronic Hamiltonian for a JT system consisting of an electronic orbital state of symmetry Σ interacting with its immediate surroundings is

$$\mathcal{H} = \frac{1}{2}\sum_{\Gamma\gamma}\left(\frac{P_{\Gamma\gamma}^2}{\mu} + \mu\omega_\Gamma^2 Q_{\Gamma\gamma}^2\right)C_{0\Gamma} + V_\Gamma \sum_{\gamma} Q_{\Gamma\gamma} C_{\Gamma\gamma} \tag{1}$$

where the $Q_{\Gamma\gamma}$ are collective vibrational coordinates of the surroundings, $P_{\Gamma\gamma}$ are the corresponding conjugate momenta and V_Γ and ω are the coupling constant and oscillator frequency respectively for the mode $\Gamma\gamma$. $C_{\Gamma\gamma}$ are the appropriate Clebsch–Gordan (CG) operators (see [7], for example) transforming like the component γ of the irreducible representation Γ such that

$$C_{\Gamma\gamma} = \sum_{\sigma_i,\sigma_j} |\Sigma\sigma_i\rangle\langle\Sigma\sigma_j|\langle\Gamma\gamma\,\Sigma\sigma_i|\Sigma\sigma_j\rangle \tag{2}$$

where σ_i and σ_j are components of Σ. The $C_{\Gamma\gamma}$ can be expressed in terms of the CG coefficients $\langle\Gamma\gamma\,\Sigma\sigma_i|\Sigma\sigma_j\rangle$ given in [7]. Also $C_{0\Gamma}$ is the identity matrix of dimension Γ. $\gamma = \theta, \epsilon, 4, 5, 6$ for coupling to the five components of the vibrational h-modes ($\Gamma = h$) and $\gamma = a, x, y, z$ for coupling to the four components of the g-modes ($\Gamma = g$).

On neglecting the kinetic energy terms in equation (1), the remaining terms in the Hamiltonian generate sets of adiabatic potential energy surfaces (APESs). These will be labelled I, where $I = 0$ corresponds to the lowest sheet. The states associated with sheet I with n phonon excitations are written as $|I, n\rangle$. In the FC approximation, the virtual transitions between the ground and excited states of the vibronic Hamiltonian, which appear in the formulae for second-order perturbation calculations, take place so rapidly that the nuclei do not move during the transition [8]. This assumption is valid if the energy gaps in the nuclear system are much larger than those present within the electronic system. This applies therefore to the systems involving strong vibronic coupling that are of interest here. The Born–Oppenheimer approximation can be then used with the factored adiabatic wavefunctions to calculate the soRFs as described in [5] for the icosahedral $T \otimes h$ JT system.

The non-Condon perturbative correction arises because the nuclei will actually move during a transition as the coupling is not infinitely strong. Coulomb attractions between the electrons and the nuclear frame will couple the two together and limit the ability of the electronic cloud to distort under perturbations. However, by allowing the nuclei to move, the polarizability of the molecular system through the electron cloud when an external perturbation is present is enhanced. This results in a considerable modification to the standard Franck–Condon diagram as transitions between the adiabatic sheets are no longer simply vertical. Transitions to and from excited vibrational levels whose energies are $n\hbar\omega_\Gamma$ (with $n = 1, 2, \ldots$) above and below the energy of the vertical transition also take place.

3. Basic formulae and definitions of vibronic reduction factors

Electronic perturbations generate first- and second-order Hamiltonians describing the coupling within the orbital state of symmetry Σ, as discussed in detail in [6] and [9], for example. The definition of the soRFs $K_M^{(2)}(\Gamma_l \otimes \Gamma_m)$ involving two perturbations, $\mathcal{H}^{(1)}(\Gamma_l)$ of symmetry Γ_l and $\mathcal{H}^{(1)}(\Gamma_m)$ of symmetry Γ_m, can be found in the general theory summarized in [10]. Their evaluation within the FC approximation for the icosahedral $T_1 \otimes h$ JT system has been described in detail in [5] and is summarized below.

Second-order perturbation theory generates a second-order Hamiltonian

$$\mathcal{H}^{(2)}(\Gamma_l \otimes \Gamma_m) = \mathcal{H}^{(1)}(\Gamma_l)G(\Sigma)\mathcal{H}^{(1)}(\Gamma_m) \tag{3}$$

where $G(\Sigma)$ is the Green operator defined by

$$G(\Sigma) = \sum_{I,n} \frac{|I, n\rangle\langle I, n|}{\Delta E^{(I,n)}} \tag{4}$$

where $\Delta E^{(I,n)}$ is the energy of the excited state $|I, n\rangle$ measured relative to the ground APES $(I = 0)$. The sum excludes the ground state $I = n = 0$.

In many systems of interest, including those to be considered here, the ground APES contains minima (or wells). To allow the system to tunnel between the wells, symmetry-adapted vibronic states can be constructed from appropriate linear combinations of the vibronic (electronic and vibrational) states in the wells. States transforming as the σ_ith component of overall symmetry Σ can be derived using projection operator techniques, for example. The resultant ground states will be written as $|0\Sigma\sigma_i\rangle$, where the '0' indicates that the oscillators in the wells are in their ground states. Following the notation developed in [10], we will write the vibronic ground states in a well p as $|\psi'_p; 0\rangle$, where the '0' again indicates that the localized oscillators in the wells are in their ground states. ψ'_p represents the vibronic state in a well expressed in a global reference frame common to all wells. The result is that the symmetry-adapted ground states can be written in the form

$$|0\Sigma\sigma_i\rangle = \sum_p \alpha_k^p |\psi'_p; 0\rangle \tag{5}$$

where the α_k^p are appropriate coefficients for well 'p'.

The soRF $K_M^{(2)}(\Gamma_l \otimes \Gamma_m)$ can then be derived from the relation

$$K_M^{(2)}(\Gamma_l \otimes \Gamma_m) = \frac{\langle 0\Sigma\sigma_i|\mathcal{L}_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m)|0\Sigma\sigma_j\rangle}{(\Sigma\sigma_i|L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m)|\Sigma\sigma_j)} \tag{6}$$

with

$$\mathcal{L}_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) = \sum_{\gamma_1,\gamma_m} C_{\Gamma_l\gamma_l} G(\Sigma) C_{\Gamma_m\gamma_m} \langle \Gamma_l\gamma_l\Gamma_m\gamma_m|M\mu\rangle \tag{7}$$

and

$$L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m) = \sum_{\gamma_l,\gamma_m} C_{\Gamma_l\gamma_l} C_{\Gamma_m\gamma_m} \langle \Gamma_l\gamma_l\Gamma_m\gamma_m|M\mu\rangle \tag{8}$$

where the label $M \in \Gamma_l \otimes \Gamma_m$ gives the overall symmetry under consideration. The states $|\Sigma\sigma_i)$, etc are combinations of pure electronic states (rather than the vibronic states involved in $|0\Sigma\sigma_i\rangle$).

As the FC approximation applies to the infinite coupling limit, we here replace the vibronic well state $|\psi'_p; 0\rangle$ in equation (5) by a product of electronic and nuclear wavefunctions with the latter function centred at the bottoms of the wells. The basic ideas can be best understood in terms of WKB wavefunctions. Detailed calculations given in [5] show that this leads to the so-called FC Green operator $G_{\mathrm{FC}}^{(p)}$ for well p in which each well is considered separately. The effective virtual transitions are vertical in an FC diagram. They originate from the vibrational ground state in one of the wells on the lowest APES and finish at the turning point of the excited vibrational state of energy $n\hbar\omega$ associated with another well in an upper sheet lying exactly above the bottom of the minimum on the lowest sheet. The expression for the soRF in the FC limit then becomes

$$K_M^{(2)\mathrm{FC}}(\Gamma_l \otimes \Gamma_m) = \sum_{p,q} \frac{\alpha_k^p \langle \psi'^p|\mathcal{L}_{M\mu}^{(2)p}(\Gamma_l \otimes \Gamma_m)|\psi'^q\rangle \alpha_l^q}{(\Sigma\sigma_i|L_{M\mu}^{(2)}(\Gamma_l \otimes \Gamma_m)|\Sigma\sigma_j)} \tag{9}$$

where $\mathcal{L}^{(2)p}_{M\mu}(\Gamma_l \otimes \Gamma_m)$ is equivalent to $\mathcal{L}^{(2)}_{M\mu}(\Gamma_l \otimes \Gamma_m)$ in equation (7) but with the Green operator replaced by $G^{(p)}_{\mathrm{FC}}$. In this approximation, the energy difference $\Delta E^{(I,p)}$ in equation (4) can be replaced by the vertical energy gap $\Delta E^{(I)}_{\mathrm{vert}}$ separating the sheets at coordinate $Q = Q_{0p}$ corresponding to the bottom of well p (which is independent of the label p). Thus the FC approximation is an accurate analytical technique in the strong coupling regime. As emphasized in [5] and [11] for the octahedral $T \otimes t_2$ and icosahedral $T \otimes h$ JT systems respectively, the underlying physics of soRFs is clearly exposed by the FC analysis.

4. Corrections from the non-Condon terms

As discussed in [6], the effect of the non-Condon (NC) terms is to give a correction $|\Delta\psi^{1p}\rangle$ to the ground state in well p which is proportional to the well displacement coordinate $q_p = Q_j - Q_{0p}$. (This correction arises from the term U_1 in the corrected potential energy given in equation (13) of [6].) Then the coordinate Q_j replaces $Q_{\Gamma\gamma}$ in equation (1). The NC perturbation also gives similar corrections to the excited well states, which also involve q_p. An additional complication is that it can cause two excited well states to be admixed but we simplify the problem in the analysis here by excluding such mixing of the excited well states.

As the orbital operators do not satisfy the closure relation after the introduction of the non-Condon corrections, the well Green operator $G^{(p)}_{\mathrm{FC}}$ must be replaced by a form derived from standard second-order perturbation theory in which the states and energy denominator include the non-Condon element. The general expression for the soRFs corrected to include NC contributions thus becomes

$$K^{(2)\mathrm{FC}}_{M,\mathrm{corr}}(\Gamma_l \otimes \Gamma_m) = \sum_{p,q} \alpha_k{}^p \frac{\langle \psi_c'^p | \mathcal{L}^{(2)p}_{M\mu,\mathrm{corr}}(\Gamma_l \otimes \Gamma_m) | \psi_c'^q \rangle}{(\Sigma\sigma_i | L^{(2)}_{M\mu}(\Gamma_l \otimes \Gamma_m) | \Sigma\sigma_j)} \alpha_l{}^q \tag{10}$$

in which $\mathcal{L}^{(2)p}_{M\mu,\mathrm{corr}}(\Gamma_l \otimes \Gamma_m)$ is now calculated using the corrected Green operator and where $|\psi_c'^p\rangle$ is the corrected new ground state in well p. In this final result, we have terms which are independent of q_p (which represent the standard FC results) together with the non-Condon correction containing terms which are of order q_p^2. Higher-order terms of order q_p^4 and $q_p^2 q_{p'}^2$ can normally be neglected.

As noted earlier, $\Delta E^I_{\mathrm{vert}}$ is proportional to the relevant JT energy E_{JT}. This in turn is proportional to the inverse square of the appropriate linear JT coupling constant V_j. Thus the non-Condon correction to the standard FC values is of the order of the inverse square of JT energy (i.e. of the order of V_j^{-4}). We also note that, even though all wells are equivalent to each other, we have nevertheless retained the labels of the individual wells in equation (10) for reasons of clarity in the following calculations.

We will now determine explicit expressions for soRFs in various icosahedral systems. For simplicity, we will restrict our calculations to cases where both perturbations have the same symmetry, namely $\Gamma_l = \Gamma_m$ $(=\Gamma)$.

5. Calculations for icosahedral orbital *G*-state systems

The work of Ceulemans and Fowler [12] provides the general theoretical background for the study of the $G \otimes (g \oplus h)$ JT system in icosahedral symmetry. This follows earlier work by Khlopin *et al* [13], Pooler [14] and by Cullerne and O'Brien [15] as reviewed in the book by Chancey and O'Brien [3]. Analytical expressions for the vibronic states and the energy spectrum were given explicitly in our earlier papers [16, 17]. In [16], the first calculations of

Table 1. The calculated values of the FC and NC contributions to the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ for the $G \otimes g$ JT system in terms of the parameters M and Γ. ($X = 1/E_{\mathrm{JT}}^{Gg}$ and $Y = \hbar\omega_g/(E_{\mathrm{JT}}^{Gg})^2$.)

M	Γ	Franck–Condon	Non-Condon
A	T_1	$-\frac{3}{8}X$	$-\frac{3}{128}Y$
A	G	$-\frac{3}{32}X$	$-\frac{9}{256}Y$
G	G	$+\frac{9}{256}X$	$-\frac{45}{2048}Y$
A	H	$-\frac{3}{8}X$	0
G	H	$-\frac{9}{32}X$	$+\frac{9}{512}Y$

foRFs and soRFs for this system were also given. Here we give the results of the more accurate calculations of the soRFs including the NC contributions.

Here we are studying an orbital G state, so the general vibronic Hamiltonian in equation (1) can be written explicitly in terms of 4×4 matrices as given, for example, in [16]. However, it is desirable to enhance the notation to give explicitly the particular JT systems involved. Thus the linear coupling constants V_g and V_h are rewritten as V_{Gg} and V_{Gh} respectively to denote that they refer specifically to the $G \otimes g$ and $G \otimes h$ JT systems respectively. The JT energies are similarly written as E_{JT}^{Gg} and E_{JT}^{Gh} respectively, while the oscillator frequencies are ω_g and ω_h respectively.

In the $G \otimes g$ subsystem, there are minima having tetrahedral ($\mathrm{T_h}$) symmetry and energy

$$E_{\mathrm{JT}}^{Gg} = -\tfrac{3}{4}k_{Gg}^2\hbar\omega_g \tag{11}$$

where $k_{Gg} = -V_{Gg}/(2\mu\hbar\omega_g^3)^{1/2}$ is a dimensionless coupling constant. In the $G \otimes h$ subsystem, the minima have trigonal ($\mathrm{D_{3d}}$) symmetry and are of energy

$$E_{\mathrm{JT}}^{Gh} = -\tfrac{3}{5}k_{Gh}^2\hbar\omega_h \tag{12}$$

where $k_{Gh} = -V_{Gh}/(2\mu\hbar\omega_h^3)^{1/2}$. (Note that the above expressions for the JT energies correct those given in [16].) In mixed systems involving coupling to both modes simultaneously, the minima arise from the most strongly coupled mode. For certain specific values of coupling in which neither mode is dominant, the JT distortion space can consist of an equipotential minimal energy trough [12, 16], but we will not consider this special case in this paper.

In the $G \otimes g$ JT subsystem, the symmetry-adapted vibronic states formed from the ground states in the five $\mathrm{T_h}$ wells consist of four degenerate ground states of G symmetry and one excited state of A symmetry, as given in [16]. Within the tetrahedral wells, the electronic G quadruplet splits into a lower A singlet separated from the upper T triplet by an energy of E_{JT}^{Gg} [12]. The results of the calculation of the soRFs as a function of the vibronic coupling coefficient k_{Gg} for this JT system are given in table 1. For clarity, the FC and NC components are listed separately. Also given in this table are the allowed overall symmetries labelled by M. Some of the results are shown graphically as a function of k_{Gg} in figure 1. However, an additional complication arises here which will be a recurring theme throughout these types of calculation. This is that the soRF $K_{Ga}^{(2)}(H \otimes H)$ has an additional label 'a' associated with the symmetry label M. This arises because the inner product of $H \otimes H$ contains two H representations. We use 'a' when the required component is obtained from the first column in the table of CG coefficients given in [7]. (Subsequently, the label 'b' will be used for components derived from the second column of the same table.)

In the case of the $G \otimes h$ JT subsystem, the symmetry-adapted states constructed from the ground states in the ten $\mathrm{D_{3d}}$ wells have symmetries G, H and A [16]. Within these wells, the

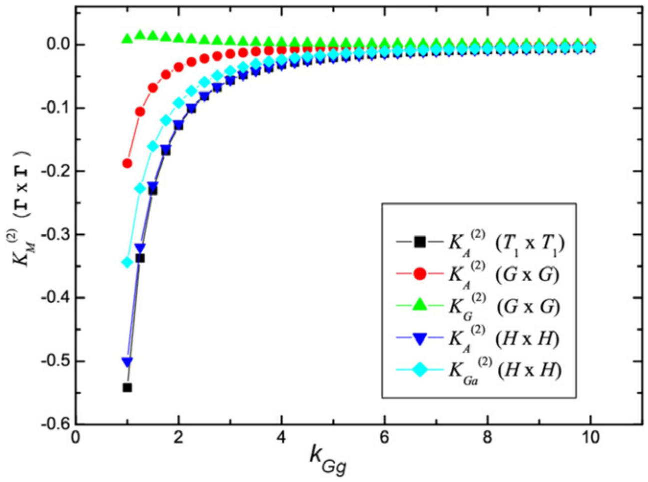

Figure 1. A plot of the calculated values of the combined FC and NC components of the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Gg} in units $\hbar\omega_g$ for the $G \otimes g$ JT system for different values of M and Γ.

Table 2. The calculated values of the FC and NC contributions to the soRFs $K_M^2(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling constant k_{Gh} for the $G \otimes h$ JT system as a function of M and Γ where $Z = 1/E_{\mathrm{JT}}^{Gh}$ and $W = \hbar\omega_h/(E_{\mathrm{JT}}^{Gh})^2$.

M	Γ	Franck–Condon	Non-Condon
A	T_1	$-\frac{33}{80}Z$	$-\frac{27}{320}W$
A	G	$-\frac{59}{160}Z$	$-\frac{33}{800}W$
G	G	$-\frac{17}{1920}Z$	$-\frac{1}{640}W$
H	G	$-\frac{113}{480}Z$	$+\frac{43}{800}W$
A	H	$-\frac{1}{5}Z$	$-\frac{273}{4000}W$
G	H	$+\frac{7}{120}Z$	$-\frac{713}{32\,000}W$
H	H	$-\frac{1}{24}Z$	$-\frac{199}{6400}W$

electronic G electronic state splits into an E doublet and two singlet states A_1 and A_2. Relative to the A_1 ground state, the excited A_2 state has an energy $\frac{2}{3}\hbar\omega_h k_h^2$ and the two E states have energies $\frac{1}{2}\hbar\omega_h k_h^2$. The corresponding soRFs are given in table 2 using the same format as in table 1. Some of the results are given in figure 2.

Generally, the FC contribution to the soRFs appearing in table 1 are relatively simple fractions, which do not always have the same sign. The NC contributions are more complicated due to the nature of the summations involved in their evaluations. They also do not always have the same signs, either as each other or as the corresponding FC contributions. The non-Condon corrections given in table 2 are also more complicated than those given in table 1 because the excited states appearing in the summations are not degenerate in this case. Clearly, all soRFs are dominated by the FC contributions which are independent of the dimensionless coupling constants. This is why the curves in the figures tend to constants in strong coupling. However, the NC contributions provide deviations from the constant values; it is these deviations that are important in this work.

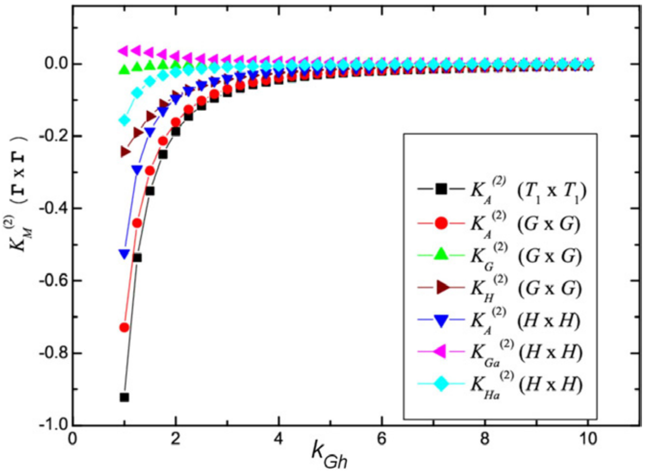

Figure 2. A plot of the calculated values of the combined FC and NC components of the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Gh} in units of $\hbar\omega_h$ for the $G \otimes h$ JT system for different values of M and Γ.

6. Calculations for icosahedral H-state orbital systems

The properties of the $H \otimes (h \oplus g)$ JT system are of much interest theoretically. The JT instabilities present were extensively studied by Ceulemans and Fowler [18]. The current authors [19] followed up their earlier modelling work [20, 21] and that of Manini and co-workers [22] by studying the motion of the system along possible tunnelling paths between different pairs of wells in the APES. Here, we are interested in calculating the soRFs for the icosahedral $H \otimes (g \oplus h)$ JT system and the corresponding JT subsystems.

For this system, the general vibronic Hamiltonian can be rewritten in terms of three 5×5 matrices as given in [23], for example, but again with an enhancement in the notation to give explicitly the particular JT systems involved. Thus the linear coupling constants V_g, V_{h_1} and V_{h_2} are rewritten as V_{Hg}, V_{Ha} and V_{Hb} respectively. Similarly, the JT energies and oscillator frequencies are similarly updated such that, for the $H \otimes g$ subsystem,

$$E_{\mathrm{JT}}^{Hg} = -\tfrac{5}{36} k_{Hg}^2 \hbar\omega_g, \tag{13}$$

for the $H \otimes Hh_a$ subsystem we have

$$E_{\mathrm{JT}}^{Hh_a} = -\tfrac{2}{15} k_{Hh_a}^2 \hbar\omega_{h_a} \tag{14}$$

and similarly for the $H \otimes Hh_b$ subsystem we have

$$E_{\mathrm{JT}}^{Hh_b} = -\tfrac{2}{5} k_{Hh_b}^2 \hbar\omega_{h_b}. \tag{15}$$

In the above equations, k_{Hg}, k_{Hh_a} and k_{Hh_b} are the relevant dimensionless coupling constants. Moate *et al* [21] gives the positions of both the trigonal D_{3d} and pentagonal D_{5d} wells. The vibronic states associated with each type of minimum are given in [20]. Thus, from the pentagonal D_{5d} minima, symmetry-adapted vibronic states of H and A symmetries are formed. Within the wells, the electronic H quintuplet in I_h symmetry splits into $A_1 \oplus E_1 \oplus E_2$ representations of D_{5d}. The A_1 state is clearly the ground state. From an analysis of the vibronic Hamiltonian, the energies of the excited E_1 and E_2 states are found to be almost the same. For our present purposes, we assume that, in keeping with other approximations, they are indeed degenerate each with relative energies equal to $2k_{Hh_b}^2/(5\hbar\omega_{h_b})$.

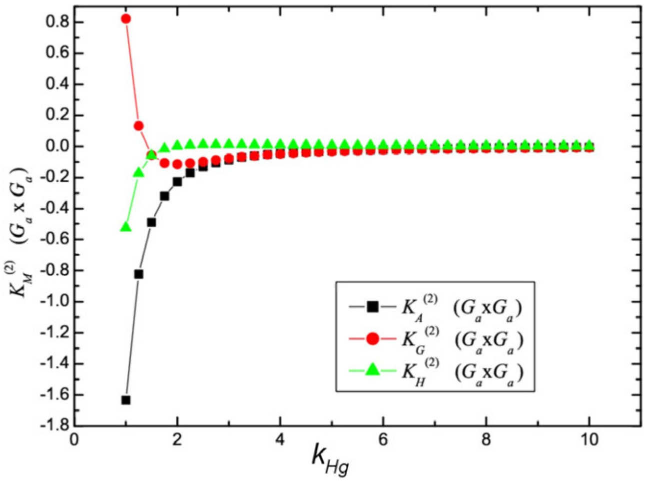

Figure 3. A plot of the calculated values of the combined FC and NC components of the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hg} in units $\hbar\omega_g$ for the $H \otimes g$ JT system for different values of M and Γ.

From the trigonal D_{3d} wells, symmetry-adapted vibronic states of H and G and A symmetries are generated. Within these wells, the electronic H quintuplet splits into a ground state of A_1 symmetry and doublet excited states of E_1 and E_2 symmetries. For the $H \otimes g$ JT subsystem, the relative energies of the E_1 and E_2 doublets are $5k_{Hg}^2/(36\hbar\omega_g)$ and $5k_{Hg}^2/(12\hbar\omega_g)$ respectively. Similarly for the $H \otimes h_a$ JT subsystem, the relative energies of the E_1 and E_2 doublets are $2k_{Hh_a}^2/(15\hbar\omega_{h_a})$ and $14k_{Hh_a}^2/(45\hbar\omega_{h_a})$ respectively.

The results of calculations for second-order RFs for the H orbital systems are tabulated in table 3 (for the $H \otimes g$ JT subsystem), in table 4 (for the for the $H \otimes h_a$ JT subsystem) and in table 5 (for the $H \otimes h_b$ JT subsystem). Some of the results are plotted in figures 3–5 respectively.

7. Discussion and conclusions

Vibronic reduction factors have been one of the most important products of JT work for almost 50 years. Much of the early work involved both theoretical and experimental studies of transition metal ion impurities, first in insulating crystals and subsequently in semiconducting crystals. These systems usually have cubic symmetry and a considerable volume of literature exists which analyses the properties of orbital doublets and triplets. There are now many examples known in which there is excellent agreement between theory and experiment, particularly for $T \otimes t_2$, $E \otimes e$ and $T \otimes (e \oplus t_2)$ JT systems [1, 2].

Some of the earliest calculations of vibronic RFs in cubic systems were undertaken by Ham [4, 25]. Comprehensive results (for cubic systems) were obtained, as discussed in [26] for example. With C_{60} ions in mind, the basic reasons for the present calculations are to assemble in one place the underlying theory for the very large number of vibronic RFs which can arise in icosahedral systems. In this way, it is hoped that a better and more complete understanding of experimental data on relevant icosahedral fullerene systems will be forthcoming. For example, such calculations may be useful in an analysis of the near-infrared absorption spectra obtained very recently from isolated C_{60}^- ions in a storage ring [27].

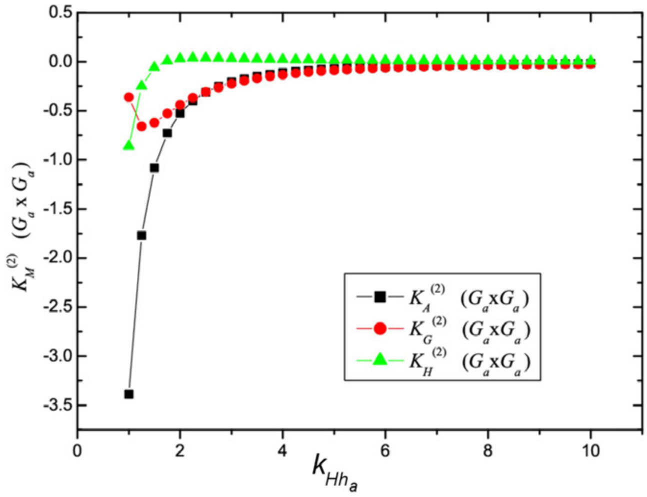

Figure 4. A plot of the calculated values of the combined FC and NC components of the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hh_a} in units $\hbar\omega_{ha}$ for the $H \otimes h_a$ JT system for different values of M and Γ.

Table 3. The calculated values of the FC and NC contributions to the soRFs $K_M^2(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hg} for the $H \otimes g$ JT system as a function of M and Γ, where $S = 1/E_{\mathrm{JT}}^{Hg}$ and $T = \hbar\omega_g/(E_{\mathrm{JT}}^{Hg})^2$.

M	Γ	Franck–Condon	Non-Condon
A	T_1	$-\frac{4}{5}S$	$-\frac{3}{10}T$
H	T_1	$-\frac{16}{45}S$	$-\frac{2}{75}T$
A	G_a	$-\frac{1}{3}S$	$-\frac{29}{120}T$
G	G_a	$-\frac{4}{9}S$	$+\frac{77}{180}T$
G	G_a	$+\frac{4}{45}S$	$-\frac{79}{450}T$
A	G_b	$-\frac{9}{5}S$	$-\frac{603}{1600}T$
G	G_b	$-\frac{4}{5}S$	$-\frac{7}{400}T$
H	G_b	$-\frac{4}{5}S$	$+\frac{29}{400}T$
A	H_a	$-\frac{14}{15}S$	$-\frac{59}{300}T$
G_a	H_a	$-\frac{74}{315}S$	$+\frac{4}{1575}T$
H_a	H_a	$+\frac{32}{9}S$	$+\frac{22}{225}T$
A	H_b	$-\frac{6}{5}S$	0
G_a	H_b	$-\frac{6}{5}S$	0
H_a	H_b	0	$+\frac{6}{25}T$

It appears that the literature contains very few references to RFs in icosahedral systems with which the results reported here can be compared, and none of these include reference to experimental data. However, our Nottingham Group and their collaborators have used a shift transformation (ST) method to deduce values for the first- and second-order RFs in the $T \otimes h$ [10], in the $H \otimes (g \oplus h)$ [19] and in the $G \otimes (g \oplus h)$ [16] icosahedral JT systems. In principle, it should be possible to compare results from the ST approach with results obtained

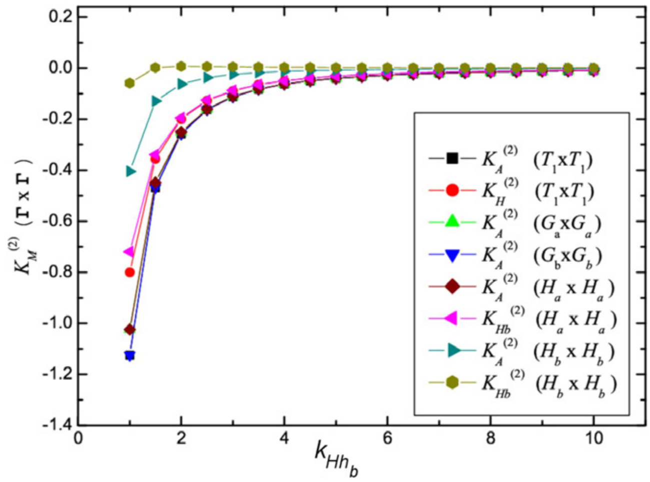

Figure 5. A plot of the calculated values of the combined FC and NC components of the soRFs $K_M^{(2)}(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hh_b} in units $\hbar\omega_{hb}$ for the $H \otimes h_b$ JT system for different values of M and Γ.

Table 4. The calculated values of the FC and NC contributions to the soRFs $K_M^2(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hh_a} for the $H \otimes h_a$ JT system as a function of M and Γ, where $L = 1/E_{\mathrm{JT}}^{Hh_a}$ and $N = \hbar\omega_{ha}/(E_{\mathrm{JT}}^{Hh_a})^2$.

M	Γ	Franck–Condon	Non-Condon
A	T_1	$-\frac{38}{35}L$	$-\frac{4911}{17\,150}N$
H	T_1	$-\frac{152}{315}L$	$-\frac{32}{3675}N$
A	G_a	$-\frac{2}{3}L$	$-\frac{2831}{10\,290}N$
G	G_a	$-\frac{8}{9}L$	$+\frac{4598}{15\,435}N$
H	G_a	$+\frac{8}{45}L$	$-\frac{92}{441}N$
A	G_b	$-\frac{18}{35}L$	$-\frac{4581}{17\,150}N$
G	G_b	$-\frac{8}{35}L$	$+\frac{122}{8575}N$
H	G_b	$-\frac{8}{35}L$	$+\frac{212}{8575}N$
A	H_a	$-\frac{34}{105}L$	$-\frac{13\,561}{51\,450}N$
G_a	H_a	$-\frac{64}{2205}L$	$-\frac{27\,788}{540\,225}N$
H_a	H_a	$+\frac{296}{315}L$	$-\frac{1304}{1575}N$
A	H_b	$-\frac{6}{7}L$	$-\frac{1263}{17\,150}N$
G_a	H_b	0	$-\frac{636}{8575}N$
H_a	H_b	$-\frac{24}{35}L$	$+\frac{1128}{8575}N$

in the present study involving the non-Condon modification of FC calculations. A comparison between the two approaches has already been made for the $T \otimes h$ JT system which has a direct relevance to the ground state of the C_{60}^- molecular anion [6]. Nevertheless, it is difficult to compare directly the new sets of results obtained here with our previous results as the FC approximation is based on an infinite strength coupling model. It is only the new non-Condon contributions which contribute as the coupling strength becomes finite. In general, it was found that the calculated values of the soRFs for the $T \otimes h$ systems were smaller in the NC

Table 5. The calculated values of the FC and NC contributions to the soRFs $K_M^2(\Gamma \otimes \Gamma)$ as a function of the vibronic coupling coefficient k_{Hh_b} for the $H \otimes h_b$ JT system as a function of M and Γ, where $U = 1/E_{\mathrm{JT}}^{Hh_b}$ and $V = \hbar\omega_{hb}/(E_{\mathrm{JT}}^{Hh_b})^2$.

M	Γ	Franck–Condon	Non-Condon
A	T_1	$-\frac{2}{5}U$	$-\frac{1}{50}V$
H	T_1	$-\frac{4}{5}U$	$-\frac{8}{25}V$
A	G_a	$-\frac{2}{5}U$	$-\frac{1}{250}V$
A	G_b	$-\frac{2}{5}U$	$-\frac{1}{250}V$
A	H_a	$-\frac{2}{5}U$	$-\frac{1}{250}V$
H_b	H_a	$-\frac{8}{25}U$	$+\frac{8}{625}V$
A	H_b	$-\frac{2}{25}U$	$-\frac{41}{1250}V$
H_b	H_b	$+\frac{8}{375}U$	$-\frac{56}{3125}V$

approach than in the ST model for the larger coupling strengths. However, in the modelling of real systems, it was suggested that the NC approach was preferable as it produced more realistic values.

We now comment, first, on the results obtained for the systems involving the G orbital. A quantitative comparison of the soRFs calculated by the two basic methods is even more difficult to make due to the increased complexities in the mathematics involved in the NC calculations. In the $G \otimes g$ JT system, the largest (negative) soRFs for $k_{Gg} > 1$ shown in figure 7 of [16] were labelled e and f; they correspond to the soRFs $K_{Ga}^{(2)}(H \otimes H)$ and $K_A^{(2)}(T_1 \otimes T_1)$ respectively. Our NC results agree with this statement. Similarly, the soRF having the smallest magnitude, labelled b in figure 7 of [16], corresponds to the soRF $K_G^{(2)}(T_1 \otimes T_1)$. This is in line with our new calculations shown in figure 1. In the $G \otimes h$ JT system, the soRF $K_A^{(2)}(T_1 \otimes T_1)$ appears to have the largest magnitude for $k_{Gh} > 1$ in both the ST method (figure 8 in [16]) and NC results given here (figure 2).

We now comment, secondly, on a few results involving the more complicated H orbital. We thus consider the $H \otimes h_b$ JT system for which the ST calculations are reported in figure 4 of [19] and the NC results here in figure 5. The soRF with the largest magnitude is $K_A^{(2)}(T_1 \otimes T_1)$ in both approaches. Similarly the soRF $K_A^{(2)}(H_a \otimes H_a)$ is equally large in both approaches.

The overall aim of this and our earlier including work [6] was to give a comprehensive account of the basic theory of soRFs in icosahedral JT systems and thus provide a framework to enable the modelling of real systems to be undertaken. As pointed out earlier, the development of the JT theory for magnetic ion impurities in semiconducting and insulating host crystals provided a most significant step in our understanding of these systems. In turn, this provided much of the basis for the manufacture of device material as well as the contributions to basic science. However, we note that many years passed before JT models in cubic systems could be used to improve our understanding of these systems. We hope that the calculations described here will generate similar benefits in our understanding of the more complex icosahedral systems such as anions and cations of the C_{60} molecule. In particular, the need for experimental data is paramount in this quest.

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