The resonant Raman spectra of several carotenoids were investigated in the past, and overtone and combination bands were assigned\(^1\); all of the latter involve intense CC stretching modes related with the effective conjugation coordinate (ECC, also denoted with \(R\); for details, see the work of Castiglioni et al.\(^2\) and the references therein). The data reported by Okamoto et al.\(^1\) reveal that mechanical anharmonicity is little, as one expects for vibrations involving the \(\pi\)-conjugated backbone of carotenoids; however, it is noteworthy that in the work of Okamoto et al.\(^1\) so many overtone and combination data were made available, in that a full set of principal and cross anharmonicity constants \(\chi_{ii}\) and \(\chi_{ij}\) were derived from experimental frequencies with great accuracy. Their values were found in the range 1–5 cm\(^{-1}\). In this work, we focus our attention on the second relevant aspect of overtones and combinations in Raman spectroscopy: the intensities, which were not discussed in the work of Okamoto et al.\(^1\) and are usually neglected also in the analysis of off-resonance Raman spectra, because of their weak signal. Indeed, we notice that the \(v^4\)-dependence of Raman intensities hampers observation of overtones, as noted, e.g. by Henry et al. in their local mode studies.\(^3\) We will tackle this problem by studying, in resonance conditions, the scattering tensor, which directly determines the intensity of higher-order Raman transitions.

The calculation of off-resonance Raman spectra of carotenoids can be carried out with density functional theory (DFT) methods,\(^4\) and it reveals a good match with the experimental counterpart (see, for instance, the case of \(\beta\)-carotene reported in Fig. 1). This is an encouraging indication that the vibrational dynamics obtained from DFT calculations is a good starting point for successive developments taking into account resonance effects.

It has been shown that in resonance conditions, higher-order Raman scattering processes are significantly enhanced compared with off-resonance conditions.\(^5\) In fact, it is not by chance that it is possible to observe and assign a considerable number of overtones and combinations in the resonant Raman spectra of several carotenoids.\(^1,4\)

The use of \(R\)-coordinate\(^2\) has proved to be useful for investigating the possible structure of carotenoid natural pigments\(^6\) and other polyenes of biological interest.\(^5,6\) On the other hand, the calculation of the Raman scattering tensor of fundamental transitions by following the same theoretical framework here considered\(^7\) was successful for other \(\pi\)-conjugated systems, namely polycyclic aromatic hydrocarbons.\(^8\) In this work, we will show that by joining the theory of \(R\)-coordinate\(^2\) with Nafie–Stein–Peticolas theory,\(^5,7\) it is possible to straightforwardly compute the resonant Raman response of \(\beta\)-carotene. In particular, the Raman intensity of each

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**Introduction**

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Theoretical model and computations

Electron–phonon coupling

In the present work, we rely on the theory describing the Raman process in terms of time-ordered diagrams, which was introduced in the seventies by Nafe et al.\(^5\) to describe interactions of electromagnetic fields and molecules. Such model makes use of a Herzberg–Teller perturbative approach, where a central role is played by the electron–phonon (e–vibration) interaction operator \(\hat{H}_{\text{e-v}}\). Of particular importance is the diagonal matrix element of the electron–phonon coupling operator, namely \(\langle \alpha | \hat{H}_{\text{e-v}} | \alpha \rangle\), the term that, at different orders and in resonance condition with excited state \(|\alpha\rangle\), is directly responsible for Raman scattering. The calculation of the electron–phonon coupling matrix element with respect to a given excited state can be most conveniently carried out by means of the transformation from normal \((Q_k)\) to Cartesian coordinates \((x_i)\) derivatives, as follows:

\[
\langle \alpha | \frac{\partial \hat{H}}{\partial Q_k} | \alpha \rangle = \langle \alpha | \sum_i \frac{\partial \hat{H}}{\partial x_i} \frac{\partial x_i}{\partial Q_k} | \alpha \rangle = \\
= \sum_i \langle \alpha | \frac{\partial \hat{H}}{\partial x_i} | \alpha \rangle \frac{\partial x_i}{\partial Q_k} L_{Rk} = g \, L_k
\]

where normal coordinates are such that \(x_i = \sum L_{ik} Q_k\). Eqn (1) allows to straightforwardly compute via time-dependent DFT the electron–phonon (e–ph) coupling matrix elements. It suffices to compute the gradient \(g_i = \langle \alpha | \frac{\partial \hat{H}}{\partial x_i} | \alpha \rangle\) of the excited state energy surface at the Franck–Condon (FC) point and consider its dot product with the eigenvector \(L_k\) of the \(k\)-th normal mode under investigation. This can be carried out without any further assumption. This approach is very promising, because, as a first step, we realized that the off-resonance intensities of the Raman fundamental transitions of \(\beta\)-carotene are well reproduced by the squares of the electron–phonon coupling parameters determined with Eqn (1) (Figure 1 and Table 1).

Effective conjugation coordinate theory permits to highlight a further aspect of the electron–phonon coupling related to vibrational displacements. In the space of nuclear coordinates, we can define a peculiar displacement direction, parallel to the gradient \(\mathbf{g}\), which is ultimately determined by ECC \((R\)-coordinate\). The unit vector \(\mathbf{u}_R\) associated to \(\mathbf{g}\) is defined as follows:

\[
\mathbf{u}_R \equiv \frac{\mathbf{g}}{||\mathbf{g}||}
\]

so that \(\mathbf{u}_R \cdot \mathbf{u}_R = 1\). The Cartesian nuclear displacements along \(\mathbf{R}\) are given by \(\mathbf{x} = \mathbf{R} \cdot \mathbf{u}_R\). Therefore, by definition, the \(R\)-coordinate recovers the strength \(||g||\) of the electron–phonon coupling:

\[
\langle \alpha | \frac{\partial \hat{H}}{\partial R_k} | \alpha \rangle = \langle \alpha | \sum_i \frac{\partial \hat{H}}{\partial x_i} \frac{\partial x_i}{\partial R_k} | \alpha \rangle = \\
= \sum_i \langle \alpha | \frac{\partial \hat{H}}{\partial x_i} | \alpha \rangle \frac{\partial x_i}{\partial R_k} = g \, u_R = ||g||
\]

By considering now a given normal coordinate \(Q_k\) whose \(R\) content is denoted \(L_{Rk} = \partial R_k / \partial Q_k\), we have

\[
\langle \alpha | \frac{\partial \hat{H}}{\partial Q_k} | \alpha \rangle = \langle \alpha | \sum_i \frac{\partial \hat{H}}{\partial x_i} L_{Rk} \frac{\partial x_i}{\partial Q_k} | \alpha \rangle = \\
= \frac{\partial R_k}{\partial Q_k} \sum_i \langle \alpha | \frac{\partial \hat{H}}{\partial x_i} | \alpha \rangle \frac{\partial x_i}{\partial R_k} = L_{Rk} g \, u_R
\]

Finally,

\[
\langle \alpha | \frac{\partial \hat{H}}{\partial Q_k} | \alpha \rangle = ||g|| L_{Rk} = \langle \alpha | \frac{\partial \hat{H}}{\partial R_k} | \alpha \rangle L_{Rk}
\]

Equation (5) can be used to provide a physical interpretation of the origin of the Raman scattering activity through electron–phonon coupling. Two important results stem from Eqn (5): The coupling of a given normal mode \(Q_k\) to the electronic excited state \(|\alpha\rangle\) is proportional to the content \(L_{Rk}\) of \(R\) in that mode \(Q_k\). The expectation value over the state \(|\alpha\rangle\) of the gradient of \(H\) with respect to \(R\) is the key factor of the e–ph coupling and represents its strength.

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Figure 1. First-order Raman spectrum of \(\beta\)-carotene: comparison of DFT calculations and experiment. Top: representation of the nuclear displacements along the \(v_1\) normal mode, computed at 1575 cm\(^{-1}\), containing the largest contribution from the \(R\)-coordinate (Table 1); the relative stretching/shrinking of CC bonds is indicated with green/blue; red arrows are proportional to the displacement vector of each atom. (a) Experimental off-resonance FT-Raman spectrum (1064 nm excitation, present work); (b) off-resonance Raman spectrum simulated with DFT (B3LYP/6-31G** calculations carried out with Gaussian09\(^{[15]}\)); (c) calculated Raman spectrum through Eqn (1): relative intensities proportional to the square of the electron–phonon coupling given by \(g \, L_k\) (see text for details; results from TD-B3LYP/6-31G** calculations). This figure is available in colour online at wileyonlinelibrary.com/journal/jrs
carried out in the past for de

We may look for a relation of
dependent nuclear displacements, which may be evaluated as

\[ E \] (i.e. at the FC point):

\[ E \] within harmonic approximation, the excited state energy surface

\[ s \] at the FC point and, similarly,\n
Through Eqn (1) (TD-B3LYP/6-31G**) compared with off-resonance

\[
\text{Table 1. Electron–phonon coupling terms for } \beta \text{-carotene computed through Eqn (1) (TD-B3LYP/6-31G**) compared with off-resonance Raman intensities (B3LYP/6-31G**, last column).}
\]

\[
\begin{array}{cccc}
\nu_i & \text{|}\alpha\text{[H} \leftarrow \text{C}0\text{]}(\%) & \text{h}_k & l_k (\AA^4/amu) \\
293 & 0.07 & 0.08 & 1834 \\
872 & 0.08 & 0.09 & 2026 \\
994 & 0.19 & 0.20 & 4776 \\
1006 & 0.28 & 0.30 & 7083 \\
1011 & 0.16 & 0.16 & 3852 \\
1029 & 2.98 & 3.11 & 73964 \\
1034 & 1.42 & 1.40 & 33373 \\
1043 & 0.87 & 0.79 & 18683 \\
1180 & 0.65 & 0.81 & 19188 \\
1198 & 7.04 & 7.82 & 186200 \\
1204 & 10.31 & 11.31 & 269180 \\
1227 & 6.48 & 6.40 & 152360 \\
1232 & 0.16 & 0.14 & 3319 \\
1257 & 1.18 & 1.08 & 25748 \\
1304 & 1.71 & 1.86 & 44319 \\
1314 & 0.57 & 0.69 & 16302 \\
1341 & 0.26 & 0.13 & 3063 \\
1351 & 0.38 & 0.59 & 14105 \\
1396 & 0.35 & 0.68 & 16102 \\
1407 & 0.05 & 0.02 & 553 \\
1435 & 0.10 & 0.20 & 4820 \\
1483 & 0.10 & 0.35 & 8401 \\
1483 & 0.07 & 0.07 & 1722 \\
1500 & 0.56 & 0.53 & 12677 \\
1501 & 2.47 & 2.10 & 50019 \\
1501 & 1.27 & 1.17 & 27918 \\
1507 & 0.44 & 0.49 & 11689 \\
1575 & 46.37 & 43.01 & 1023600 \\
1585 & 8.91 & 8.77 & 208660 \\
1643 & 1.60 & 1.51 & 36046 \\
1653 & 1.89 & 2.53 & 60101 \\
Total & 98.97 & 98.39 & \\
\end{array}
\]

The sum of percent values over all normal modes is 100. We report results only for modes with strong enough electron–phonon and Raman intensity (relative electron–phonon coupling larger than 0.05%).

The \( \mathcal{R} \)-coordinate is defined by a set of collective inter-dependent nuclear displacements, which may be evaluated as shown in the following. We may look for a relation of \( \mathcal{R} \) with the displacement between ground and excited state minima, as carried out in the past for defining \( \mathcal{R} \) in \( \pi \)-conjugated systems (see the work of Castiglioni et al.[2] and the references therein).

Within harmonic approximation, the excited state energy surface \( E_\alpha(x) \) can be expanded around the minimum of the ground state (i.e. at the FC point):

\[
E_\alpha(x) = E_\alpha^0 + h\Omega_{xx}^0 + \sum_i g_i^\alpha x_i + \frac{1}{2} \sum_i \sum_j f_{ij}^\alpha x_i x_j
\] (6)

where \( g_i^\alpha = \langle \alpha | \frac{\partial^2 H}{\partial x_i^2} | \alpha \rangle \) is the gradient of the excited state energy surface at the FC point and, similarly, \( f_{ij}^\alpha \) are the matrix elements of the Hessian of the excited state energy surface; \( h\Omega_{xx}^0 \) is the vertical transition energy. The minimum of the excited state surface satisfies \( \partial E_\alpha/\partial x_i = 0 \); hence, its ‘multi-dimensional’ distance \( |x_i| \) from the FC point has to satisfy the following equation:

\[
g_i^\alpha = \frac{\sum j f_{ij}^\alpha x_j}{\sum j f_{ij}^\alpha}
\] (7)

The solution to Eqn (7) defines the displacement from the FC point to the excited state minimum or, equivalently, the distance of ground and excited state minima \( \Delta x_i^{\leftrightarrow} \), that is,

\[
x_i = \Delta x_i^{\leftrightarrow} = -\sum_j \{ \alpha \} f_{ij}^\alpha g_j^\beta
\] (8)

Or equivalently

\[
g_i^\alpha = -\sum_j f_{ij}^\alpha \Delta x_j^{\leftrightarrow}
\] (9)

In vector notation, \( \mathbf{g}^\alpha = -\mathbf{f} \Delta \mathbf{x}^{\leftrightarrow} \). If one considers the unit vectors associated to the two quantities \( \mathbf{g}^\alpha, \Delta \mathbf{x}^{\leftrightarrow} \), one obtains a collective nuclear displacement suitable for defining the \( \mathcal{R} \)-coordinate of the \( \pi \)-conjugated system. On the basis of Eqn (9), one concludes that \( \mathbf{g}^\alpha \) or \( \Delta \mathbf{x}^{\leftrightarrow} \) essentially provides the same displacement coordinate when the force constant matrix \( \mathbf{f} \) does not induce any substantial ‘rotation’ to the direction of \( \Delta \mathbf{x}^{\leftrightarrow} \) vector. This happens when \( \mathbf{g}^\alpha \) or \( \Delta \mathbf{x}^{\leftrightarrow} \) is close enough to some eigenvector of the \( \mathbf{f} \) matrix. The situation for \( \beta \)-carotene has been checked with time-dependent DFT calculations carried out on the lowest dipole-allowed excited state \( |\alpha\rangle \). The gradient at the FC point, the optimized structure and the ‘force constant matrix’ of the excited state have been computed with TD-B3LYP/6-31G** method, providing \( \Delta \mathbf{x}^{\leftrightarrow}, \mathbf{g}^\alpha \) and \( \mathbf{f} \).

The direct comparison of \( \Delta \mathbf{x}^{\leftrightarrow} \) with \( \mathbf{g}^\alpha \) is potentially plagued with spurious roto-translations or large amplitude motions of the molecule upon excitation, which hinder the straightforward evaluation of the vibrational contribution to \( \Delta \mathbf{x}^{\leftrightarrow} \). Hence, we adopt an indirect approach, which consists in considering Eqn (9) and checking whether the components of normalized \( \mathbf{g}^\alpha \) (\( \mathbf{u}_R \)) are close to those of some eigenvector of the \( \mathbf{f} \) matrix, i.e. we

\[
\begin{align*}
\mathbf{g}_i^\alpha + \sum_j f_{ij}^\alpha x_j &= 0 \\
\mathbf{g}_i^\alpha &= -\sum_j f_{ij}^\alpha \Delta x_j^{\leftrightarrow}
\end{align*}
\]

**Figure 2.** Correlation between the components of the normalized \( \mathcal{R} \) vector (\( \mathbf{u}_R = \mathbf{g}^\alpha/||\mathbf{g}^\alpha|| \)) and those of the normalized vector obtained from the matrix product \( \mathbf{f} \mathbf{u}_R \) (from TD-B3LYP/6-31G** calculations). Red points indicate the components of the vectors pertaining to carbon atoms, while blue points are relative to hydrogen atoms, which are unaffected by a displacement along the \( \mathcal{R} \)-coordinate. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs
checked if \( u_R \) is parallel to \( f^\dagger u_R \). Figure 2 shows the components of the unit vector defining the ECC coordinate, \( u_R \), against the components of the vector \( f^\dagger u_R \) (normalized as well). It is clear that the two vectors are parallel to a good approximation; hence, the gradient \( g^\dagger \) (\( R \)-coordinate) is very close to an eigenvector of the force constant in the excited state. In conclusion, on the basis of Eqn (9) and the results summarized in Fig. 2, we deduce that for the lowest lying bright state of \( \beta \)-carotene, the gradient \( g^\dagger \) and the displacement \( \Delta x^{\alpha \rightarrow \nu} \) are parallel vectors, to a good approximation. Thus, in principle, both quantities can be used to define the \( R \)-coordinate, i.e. one can either calculate the gradient at the FC point or optimize the excited electronic state and compute the geometry difference with respect to the ground state. These two approaches can be used to define the \( R \)-coordinate in other carotenoids and oligenes and in general in other molecular systems.

**Raman scattering**

The aforementioned discussion has highlighted the key role of electron–phonon coupling in resonant Raman spectroscopy of \( \pi \)-conjugated molecules. We consider now the expressions given in the work of Nafe et al.\(^{[5]} \) for resonant Raman intensities of overtones and combinations. We aim at providing working equations suitable for numerical evaluation, on the basis of quantities directly obtained from quantum chemical calculations. Neglecting the contributions from hot band transitions and anti-Stokes processes and assuming that the interaction process consists in the creation of \( n \) vibrational quanta, each one with energy \( \hbar \omega \), in \( n \) successive steps (promoted by time-ordered radiation field–molecule interaction by the first-order perturbative terms of Eqns (1–5) and as presented in the first two schemes of Fig. 3(a)\(^{[5,9]} \)), the Raman intensity of a generic \( n \)-th overtone of a given normal mode \( Q \) can be written as follows:

\[
I_n = |\langle 0|Q|1\rangle\langle 1|Q|2\rangle\ldots(n - 1|Q|n)|^2 \times \frac{\left|\langle g|\mu_1|a\rangle\left(\frac{\partial}{\partial x^a}\right)\langle a|\mu_1|g\rangle\right|^2}{\prod_{k=0}^{n-1}(E_a - E_g - \hbar\omega_k + k\hbar\Omega + \Delta)}
\]  

In the work of Nafe et al.\(^{[5]} \), it is shown how the denominator of Eqn (10) stems from the use of time-ordered diagrams in the context of perturbation theory describing vibronic interactions\(^{[7]} \), through \( \langle \partial H/\partial Q_i \rangle_Q \) (i.e. Herzberg–Teller). Hence, the unperturbed energy differences \( E_a - E_g \) are the vertical transition energies computed at the unperturbed nuclear equilibrium of the ground state \( (Q=0) \). Dimensional analysis of the right-hand term of Eqn (10) reveals a quantity commensurate to the square of a polarizability (i.e. the square of a transition dipole moment, squared, divided by an energy). This is expected on the basis of the general quantum expression for Raman scattering (Kramers–Heisenberg–Dirac) given, for instance, in the work of Albrecht\(^{[10]} \):

\[
I_{\nu \rightarrow \nu} = \frac{2\pi^3}{3^3 c^4} I_0 (v_0 + v_1 - v_2)^4 \sum_{\sigma} |\langle \sigma|\varphi_{\nu \rightarrow \nu} \rangle|^2
\]  

The quantum mechanical term \( |\langle \sigma|\varphi_{\nu \rightarrow \nu} \rangle|^2 \) directly relates to molecular vibrational and electronic structure (i.e. resonances) and dimensionally corresponds to a polarizability. Its expression involves the product of transition dipole moments divided by transition energies.

The square of the product of integrals over vibrational wavefunctions in Eqn (10), i.e. \( |\prod_{k=1}^{n}(k-1|Q|k)|^2 \), can be evaluated within mechanical harmonic approximation by means of popular tables of integrals involving Hermite polynomials, as those given in the study of Wilson et al.\(^{[11]} \). The result is

![Figure 3](image)  
**Figure 3.** Time-ordered diagrams relative to Raman process involving (a) overtones of a given mode \( Q \); (b) combination of two modes \( Q_i \) and \( Q_j \) and (c) three-quanta combinations over two normal modes. Diagrams have been taken and adapted from the study of Nafe et al.\(^{[5]} \).
For overtones (first two schemes in Fig. 3(a)),

\[
\begin{align*}
I_{nk} & \propto n! \left( \frac{\hbar}{2\Omega} \right)^n \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^n \\
& = n! \left( \frac{\hbar}{2\Omega} \right)^n \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^n \left( \frac{\hbar}{\Omega} \right)^2
\end{align*}
\]  

For combination of two quanta over two normal modes \(Q_n\) and \(Q_k\), one has (Fig. 3(b))

\[
\begin{align*}
I_{n+k} & \propto \left( \frac{\hbar}{2\Omega} \right)^2 \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \left( \frac{\hbar}{\Omega} \right)^2 \\
& = \left( \frac{1}{2\hbar\Omega_k} \right)^2 \left( \frac{1}{2\hbar\Omega_n} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_n}{\Omega} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^2
\end{align*}
\]  

Evaluation of resonant Raman intensities of \(\beta\)-carotene

To numerically evaluate relative Raman intensities for fundamentals, overtones and combinations, we simplify the aforementioned expressions, assuming resonance condition, \(\hbar\omega_1 = E_a - E_g\) and factoring out transition dipoles. Furthermore, \(\langle \alpha | \partial H / \partial Q_1 | \alpha \rangle = \mathbf{g} \cdot \mathbf{L}_n\), where \(\mathbf{g}\) is the gradient at the FC point on the excited state relevant for the resonance condition and \(\mathbf{L}_n\) are the nuclear displacements associated to the normal coordinate \(Q_n\). For fundamental Raman transitions, this gives the following:

\[
I_\alpha \propto \frac{\hbar}{\Omega} \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^2 = \frac{1}{2\hbar\Omega_k} \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^2
\]  

Three quanta Raman transitions over two normal modes \(Q_n\) and \(Q_k\) (Fig. 3(c)) give rise to

\[
\begin{align*}
I_{n+k} & \propto \left( \frac{1}{2\hbar\Omega_n} \right)^2 \left( \frac{1}{2\hbar\Omega_k} \right)^2 \left( \frac{\hbar}{\Omega} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_n}{\Omega} \right)^2 \\
& + \left( \frac{1}{2\hbar\Omega_n} \right)^2 \left( \frac{1}{2\hbar\Omega_k} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^2 \\
& = \left( \frac{1}{2\hbar\Omega_n} \right)^2 \left( \frac{1}{2\hbar\Omega_k} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_n}{\Omega} \right)^2 \left( \frac{\mathbf{g} \cdot \mathbf{L}_k}{\Omega} \right)^2
\end{align*}
\]
Three quanta Raman transitions over three normal modes \((Q_n, Q_k \text{ and } Q_l)\) (scheme not reported) give rise to

\[
\hbar \cdot \nu \propto \left( \frac{1}{2\hbar \Omega_{n}} \right) \left( \frac{1}{2\hbar \Omega_{k}} \right) \left( \frac{1}{2\hbar \Omega_{l}} \right) \times \left\{ \begin{array}{l}
\langle \hbar g L_{n} \rangle \langle \hbar g L_{k} \rangle \langle \hbar g L_{l} \rangle \\
\frac{1}{\Pi \left( \Pi + h \Omega_{n} \right) \left( \Pi + h \Omega_{k} + h \Omega_{l} \right) \left( \Pi + h \Omega_{n} + h \Omega_{k} + h \Omega_{l} \right) \left( \Pi + h \Omega_{n} + h \Omega_{k} + h \Omega_{l} \right)}
\end{array} \right\}
\]

Dimensional analysis reveals that \(\hbar \cdot \nu\) has units of \([\text{energy}]^{1/2}\).\(^2\) By consequence, the dimensions of the right-hand-side of Eqns (15–19) are all \([\text{energy}]^{3/2}\), as expected on the basis of the discussion that closely follows Eqn (10).

By making use of Eqns (15–19), on the basis of results from DFT calculations (as mentioned earlier), we have computed resonant Raman intensities of fundamentals, overtones and combinations of \(\beta\)-carotene. These data have been used to produce a simulated Raman spectrum, which is reported in Fig. 4 and compared with experimental data taken from the study of Okamoto et al.\(^{[1]}\).

**Discussion of the results and conclusions**

The results of Fig. 4 are pretty encouraging for two reasons:

1. Within each one of the four manifolds of Raman resonant features defined by Okamoto et al.\(^{[1]}\), the agreement between experiments and theory/computations is pretty good (looking at Fig. 4, the manifolds contain respectively the following: the fundamentals, between 1000 and 1600 cm\(^{-1}\); the first overtones \((2\nu_i)\) plus two-quanta combinations, between 2000 and 3200 cm\(^{-1}\) a set of higher-order combinations involving three quanta, between 3200 and 4200 cm\(^{-1}\); and the second overtone of \(\nu_1\) \((3\nu_1)\) plus other combinations, between 4200 and 5000 cm\(^{-1}\)).

2. Most importantly, these nice results are arrived at by just calculating the gradient \(g\) or other associated quantities such as \(uR\), which means that a common mechanism for electron–phonon coupling explains the majority of intensity data of Fig. 4, and what really counts to confer intensity to fundamental, overtone or combination features in resonance Raman spectra is the participation of the \(R\)-coordinate in the normal modes involved in the transitions under observation.

However, looking more closely, one realizes that the agreement of theory to experiment is not 100% perfect, and this will require some further effort to obtain an impeccable interpretation of the data. As a first step in this direction, we may notice that the features observed at 3048, 3319 and 4050 cm\(^{-1}\) are underestimated by the present calculations. The first and last bands are attributed to \(2\nu_1\) and to \(2\nu_1 + \nu_2\), respectively. A possible source of error in the evaluation of intensities is the neglect in our approach of one basic interaction event included in

---

\(^{[2]}\)This is easily proved because Cartesian displacements along the \(k\)-th normal mode satisfy \(\Delta x_{k} = L_{k} \Delta Q_{k}\) and the normal coordinate \(Q_{k}\) is mass-weighted and hence has dimension of \([\text{length} \cdot \text{mass}]^{1/2}\). Hence, \(L_{k}\) has dimension of \([\text{mass}]^{-1/2}\).

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**Figure 4.** Resonant Raman spectrum of \(\beta\)-carotene. Comparison of experimental data recorded by Okamoto et al.\(^{[1]}\) with excitation at 457.9 nm (black line) and calculated data by the present theoretical analysis (red and orange lines). Wave numbers from DFT have been scaled by 0.965; strict mechanical harmonic approximation has been used to compute the wavenumbers of overtones and combinations based on fundamentals. The value for numerical calculations of Raman intensities is 250 cm\(^{-1}\); the pattern of relative Raman intensities does not sensibly change for \(\Gamma < 1000 \text{ cm}^{-1}\). The orange line shows the simulated Raman spectrum magnified four times. Assignment of overtones and combinations follows the one given in the study of Okamoto et al.\(^{[2]}\). The experimental peak at 4831 cm\(^{-1}\) is not present in the simulations because we have not considered here fourth-order Raman processes. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs
the original derivation of Nafie et al.,\textsuperscript{[5]} namely the one involving the direct generation of an overtone vibration, which we recall in Fig. 3(a), last column, pasting the picture from Nafie et al.\textsuperscript{[5]}

The intensity associated to such event in resonance condition \((\hbar \omega_1 = E_a - E_g)\) is

\[
I_{2k} \propto |\langle 0 | Q_j^2 | 2 \rangle|^2 = \frac{1}{4} \prod_{n=1}^k \left( \frac{\omega_{n+1} - \omega_n}{\omega_n} \right)^4 \left( \frac{\omega_{n+1} + \omega_n}{\Omega_n} \right)^2
\]

(20)

Indeed, in the time-ordered scheme, such term arises because of a first-order event (such as the one promoting fundamentals) and is caused by second-order perturbative interaction, \(\frac{\partial^2 \mu}{\partial Q^2} \langle Q \rangle^2\).\textsuperscript{[9]} The numerator of the last factor in Eqn (20) contains the square of the vibrational energy of mode \(Q_1\) in the electronic excited state \(|\alpha\rangle\), which we may indicate as \(\hbar \Omega_1\). Comparison of Eqn (16) for \(n = 2\) and of Eqn (20) shows that the two terms are in the following ratio:

\[
\frac{I_{2k \Delta n}}{I_{eq \Delta n}} \propto \left( \frac{\hbar \Omega_1}{\hbar \Omega_1 + \Omega_2} \right)^4 \left( \frac{\hbar \Omega_1 + \Omega_2}{\hbar \Omega_1} \right)^2
\]

(21)

This means that the importance of the neglected term increases with \(\Omega_1\) which may explain why \(\chi_2\) overtones and combination involving \(\nu_2\), the largest in the spectrum of the fundamental manifold, should have a larger intensity than estimated in the present model.

Because of the theoretical model we have presented earlier, we recognize that the observation of Raman overtones in resonance conditions is not typical of \(\beta\)-carotene. Indeed, not only Tasumi’s group did observe the same phenomena in Raman spectra of other \(\pi\)-conjugated and variously substituted or terminated polyenes\textsuperscript{[11]} but also C\textsuperscript{i} et al.\textsuperscript{[15]} studied hexatriene and found that, by progressively tuning to resonance the excitation radiation, overtone features increase in Raman intensity more evidently than fundamentals.

For this reason, we applied the Nafie–Stein–Petricolas theory also to hexatriene, with excellent results, as reported in the Supporting information.

Furthermore, the results presented here can find application to other systems than carotenoids, for which electron–phonon processes are relevant as, for instance, carbon nanotubes and graphene.\textsuperscript{[13,14]}

The fact that the intensities of the overtones can be easily recorded in resonance condition may be rationalized by simple DFT calculations reported in Fig. 5 (for the sake of consistency with the rest of this work, we kept B3LYP/6-31G** level of theory).

There, we demonstrate that divergences in the trace of the polarizability tensor of hexatriene, because of resonance with radiation of wavelength in the interval 240–290 nm, are met with displacements along the strongest Raman active CC stretching mode (TD-B3LYP/6-31G** locates resonance with \(S_1\) at about 255 nm). Because overtones imply large displacements, these calculations further justify the special connection of overtones to resonance. In fact, large amplitude displacements \(\Delta Q\), when close to resonance conditions, allow probing the whole singular region in the \(a(Q)\) diagram (Figure 5). In a polarizability derivative context for Raman intensity, this would imply exploring a region where the linear approximation \(a(Q) = a_0 + \langle \partial a/\partial Q \rangle_{Q=Q0} Q\) is no more tenable; hence, overtones due to higher polarizability derivatives would be straightforwardly implied.

\[\text{Figure 5.} \text{ Calculated value of isotropic polarizability of hexatriene versus the displacement } \Delta Q \text{ along the strongest Raman mode (computed at } 1708 \text{ cm}^{-1}, \text{ nuclear displacement pattern reported at the top of figure) in presence of electromagnetic field of wavelength in the interval 200–600 nm (B3LYP/6-31G** calculations). Units of the color bar are nanometer. The data corresponding to the resonance predicted by TD-B3LYP/6-31G** (255 nm) are plotted with open circle symbols. For the sake of understanding, at the maximum displacement } \Delta Q \text{ of } +0.2 \text{ Åamu}^{-1/2}, \text{ the central C–C bond elongates from its equilibrium value of } 1.352 \text{ Å to the value of } 1.408 \text{ Å. This figure is available in colour online at wileyonlinelibrary.com/journal/jrs.}\]

\[\text{Appendix: A}\]

By referring to the well-known integrals over the eigenfunctions of the harmonic oscillator (see, for instance, the work of Wilson et al.\textsuperscript{[11]}), it is straightforward to derive the following result:

\[
\langle 0 | Q | 1 \rangle \langle 1 | Q | 2 \rangle \cdots \langle n-1 | Q | n \rangle = \prod_{k=0}^{(n-1)} (k + 1) = \prod_{k=0}^{(n-1)} \left( \frac{\hbar}{2 \Omega} (k + 1) \right)^{1/2}
\]

(A1)

Hence, the square of the modulus becomes

\[
|\langle 0 | Q | 1 \rangle \langle 1 | Q | 2 \rangle \cdots \langle n-1 | Q | n \rangle|^2 = \prod_{k=0}^{(n-1)} \left( \frac{\hbar}{2 \Omega} (k + 1) \right)^{1/2} = \left( \frac{\hbar}{2 \Omega} \right)^n \prod_{k=0}^{(n-1)} (k + 1) = \left( \frac{\hbar}{2 \Omega} \right)^n \times 2 \times \cdots \times (n - 1) \times n = n! \left( \frac{\hbar}{2 \Omega} \right)^n
\]

(A2)

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References


Supporting information

Additional supporting information may be found in the online version of this article at the publisher’s web site.