

Dipole and rotational strengths for overtone transitions of a C_2 -symmetry HCCH molecular fragment using Van Vleck perturbation theory

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Contact transformation theory up to second order is employed to treat CH-stretching overtone transitions and to calculate dipole and rotational strengths. A general Hamiltonian describing two interacting CH-stretching oscillators is considered, and the Darling–Dennison resonance is appropriately taken into account. The two CH bonds are supposed to be dissymmetrically disposed, so as to represent a chiral HCCH fragment, endowed with C_2 symmetry. Analytical expressions of transition moments and dipole and rotational strengths are given in the hypothesis of general electric and magnetic dipole moments with quadratic dependence on coordinates and momenta. Dipole and rotational strengths are then calculated together with frequencies for the fundamental and first three overtone regions in the simplifying hypothesis of the valence optical approach on the coupled-oscillator framework. Simplified analytical expressions thereof in the relevant parameters are presented. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504705]

I. INTRODUCTION

A renewed interest in measuring vibrational circular dichroism (VCD) spectra in the CH stretching overtone region^{1–3} has raised the necessity of calculating overtones' rotational strengths.⁴ For this reason we have undertaken the study of a simplified model consisting of two coupled oscillators described by a two-degrees-of-freedom Hamiltonian including Darling–Dennison (DD) terms.⁵ This kind of dynamical model has been demonstrated to be quite appropriate to study both fundamental and overtone transitions, and has been extensively studied in the literature by means of second-order perturbation theory,⁶ by integration of classical equations of motion, and semiclassical quantization of trajectories.^{4,7–9} We adopt here the method of Van Vleck contact transformations, for the main reason that these transformations can be easily applied to operators, permitting one to examine the analytical expressions of the electric and magnetic dipole moments treated at any desired order.

The contact transformation formalism was originally developed for accurately calculating frequencies and for interpreting high-resolution spectra of molecules in the gas phase.^{10–13} Afterwards, it was also adapted and used for calculating dipole and rotational strengths in the infrared range.^{14–16} Expressions for dipole and rotational strengths for overtone transitions have been obtained by Bak *et al.*¹⁷ and Polavarapu¹⁸ for a single chiral oscillator and by ourselves⁴ for a system of two oscillators with strong simplifying assumptions that will be abandoned in this paper. More recently, the same perturbative method has been applied to study vibrational manifolds, which are important for overtone spectroscopy, with quite high orders of perturbative terms and increasing number of degrees of freedom.¹⁹

We have limited ourselves here to a simple two-oscillator model and to low perturbative orders to handle simple analytical results. We have studied the system of two

interacting CH stretches in a dissymmetric HCCH molecular fragment (Fig. 1), with the additional requirement that it possess a C_2 -symmetry axis bisecting the CC bond; this requisite does not prevent it from exhibiting optical activity. Our choice is motivated by the fact that it is the simplest coupled-oscillator model and is still extensively applied for the interpretation of spectra of CH stretching vibrations in many chiral molecules.^{20–23} The model is adequate when the CH stretchings can be regarded as dynamically and possibly electrically (as we will discuss later) isolated from other vibrational modes. If the valence angles and the dihedral angle in this fragment are fixed, two normal modes are present, one being symmetric and the other antisymmetric with respect to the C_2 -symmetry axis: let the corresponding normal-mode dimensionless coordinates and conjugated momenta be denoted by q_s , p_s and q_a , p_a , respectively. Let the corresponding frequencies in wave number units be ω_s and ω_a , respectively. Following the notation of Ref. 4, the general Hamiltonian possessing C_2 symmetry at fourth order is

$$H = H_0 + \varepsilon H_1 + \varepsilon^2 H_2, \quad (1)$$

where

$$H_0 = (hc/2) \{ \omega_s [(p_s/\hbar)^2 + q_s^2] + \omega_a [(p_a/\hbar)^2 + q_a^2] \}, \quad (1')$$

$$\varepsilon H_1 = hc [K_{sss} q_s^3 + K_{saa} q_s q_a^2], \quad (1'')$$

$$\varepsilon^2 H_2 = hc [K_{ssss} q_s^4 + K_{aaaa} q_a^4 + K_{ssaa} q_s^2 q_a^2]. \quad (1''')$$

In Ref. 4 drastic assumptions regarding anharmonic force constants were made; i.e., only diagonal cubic and quartic terms K_{iii} and K_{iiii} were assumed to be different from zero (the index i denotes a generic normal mode); this simplification allows one to avoid the problem of resonances and assimilates the many-oscillator problem to the one of a single oscillator. We stated, however, that the inclusion of the inter-

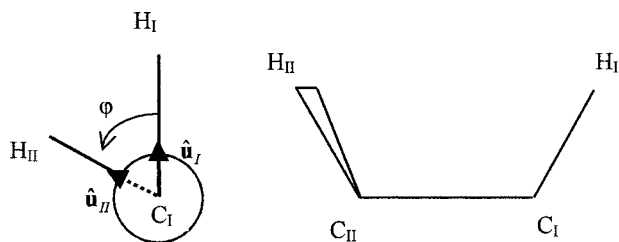


FIG. 1. Definition of the $H_I C_I C_{II} H_{II}$ dissymmetric system and of dihedral angle φ between planes $H_I C_I C_{II}$ and $H_{II} C_I C_I$: front view (Newman projection) and side view.

action term K_{ijj} ($i \neq j$) is necessary, as had been pointed out by many authors,^{24–27} in order to account for the transition from the normal-mode regime to the local-mode regime.²⁸ The inclusion of the K_{ijj} term is essential to demonstrate the equivalence of a normal-mode Hamiltonian with anharmonic interactions, like the one we use here, to the Hamiltonian of harmonically coupled anharmonic oscillators (for a review, see Ref. 6).

Hamiltonian (1) coincides with the one that Mills and Robiette used for water in normal coordinates.²⁶ The equivalence between the normal-mode scheme and the local-mode scheme, proved by way of a variational perturbative treatment, implies the existence of appropriate relations between the parameters ω_0 , χ of the bond Morse potential in local coordinates and the anharmonic coefficients K_{ijk} , K_{ijkl} [these relations are reported for completeness in Appendix A, Eq. (4)]. Appendix A comprises the general expressions of the frequencies ω_s and ω_a and of the anharmonic cubic and quartic force constants for two interacting Morse oscillators. In the present work, the contact transformation approach has to be carried out at least to second order (two contact transformations) and in resonance form, since the resonance appears at second order. In fact, we shall show that these contact transformations at second order give the same matrix elements for the Hamiltonian and, accordingly, the same energy levels as obtained in the perturbative treatment by Mills and Robiette.²⁶

II. DETERMINATION OF CONTACT TRANSFORMATIONS

Let us briefly recall the contact transformation procedure to illustrate the notation that we are going to use and to introduce all the elements needed to obtain the transformed operators.

The first contact transformation is generated by an operator $T_1 = \exp(i\epsilon S_1) = 1 + i\epsilon S_1 + \dots$ that acts on a generic operator \hat{f} analogously to the Lie transformations^{29–31} in classical mechanics; formally, one can express the transformed operator \hat{f}' as

$$\hat{f}' = T_1 \cdot \hat{f} \cdot T_1^{-1} = \sum_s \frac{(i\epsilon)^s}{s!} [S_1, \hat{f}]^s, \quad (2)$$

with $[S_1, \hat{f}]^s = [S_1, [S_1, \dots, [S_1, \hat{f}]]]$; that is to say, the commutation $[S_1, \dots]$ is applied s times on \hat{f} . When this transformation is applied to H , it gives

$$H' = T_1 \cdot H \cdot T_1^{-1} = H'_0 + \epsilon H'_1 + \epsilon^2 H'_2 + \dots \quad (3)$$

The requirement that one imposes in order to determine the generating function S_1 is that the off-diagonal elements of $\epsilon H'_1$, evaluated on the product harmonic oscillator eigenfunction basis, vanish at first order. We denote by $|n_s, n_a\rangle_n$ the normal-mode basis (uncoupled harmonic oscillators). This is exactly equivalent to saying that the eigenfunctions of the complete Hamiltonian H are obtained at first order in ϵ by $T_1^{-1} |n_s, n_a\rangle_n$. Since H_1 contains odd powers of the coordinates, the requirement ${}_n \langle n'_s, n'_a | H'_1 | n_s, n_a \rangle_n = 0$, if $n'_s, n'_a \neq n_s, n_a$, corresponds to imposing that $i[S_1, H_0] = -H_1$ and to reducing Eq. (2) to the following conditions:

$$H'_0 = H_0, \quad (4)$$

$$H'_1 = 0, \quad (4')$$

$$H'_2 = H_2 + \frac{i}{2} [S_1, H_1]. \quad (4'')$$

The transformation S_1 obtained in this way contains new terms with respect to those of Ref. 4, due to the presence of cubic “nondiagonal” perturbative terms, and S_1 turns out to be¹⁰

$$S_1 = S^{sss} p_s^3 + (1/2) S_{ss}^s (p_s q_s^2 + q_s^2 p_s) + S^{saa} p_s p_a^2 + (1/2) S_{sa}^a q_s (p_a q_a + q_a p_a) + S_{aa}^s p_s q_a^2. \quad (5)$$

The five coefficients depend on the cubic force constants K_{sss} and K_{saa} as reported in Appendix A.

With the aim of treating contact transformations at successive orders and of calculating transition moments for electric and magnetic dipole moments, we used the algebraic manipulator MAPLE.³² This package gives one the opportunity to work with noncommutative algebras and has allowed us to easily evaluate complicated matrix elements of harmonic-oscillator eigenfunctions.

As indicated before, it is essential to consider at least a second contact transformation, thus diagonalizing the Hamiltonian at second order. There are many reasons to go to second order. The first reason is that the anharmonic behavior of bond-type oscillators is well described by cubic and quartic force constants; stopping at first order permits one to deal with just cubic force constants and does not allow one to obtain energy levels in correspondence with those spectroscopically observed for the isolated oscillator and to give a description equivalent to the well-accepted models present in the literature.³³ Second, in the case of more than one oscillator, the importance of the DD (Refs. 5, 25, and 26) interaction terms has been recognized to cause a 2:2 resonance and thus one must go to second order. Last but not least, mechanical and electrical anharmonicities beyond first order are essential for an acceptable description of overtone absorption intensities.^{34–36}

The implementation of procedures based on MAPLE leads first to determine the transformation $T_2 = \exp(i\epsilon^2 S_2) = 1 + i\epsilon^2 S_2 + \dots$ that diagonalizes the Hamiltonian terms at next order. In analogy to Eq. (2) one obtains, for a generic \hat{f}' ,

$$\hat{f}^+ = T_2 \cdot \hat{f}' \cdot T_2^{-1} = \sum_S \frac{(i\varepsilon^2)^S}{s!} [S_2, \hat{f}']^S. \quad (6)$$

Being $H^+ = H_0^+ + \varepsilon \cdot H_1^+ + \varepsilon^2 \cdot H_2^+$, we obtain

$$H_0^+ = H'_0, \quad (7)$$

$$H_1^+ = H'_1, \quad (7')$$

$$H_2^+ = H'_2 + i[S_2, H_0]. \quad (7'')$$

As well described in Ref. 11, S_2 must be determined by the requirement that off-diagonal terms be eliminated from H_2^+ . Beside that, one has to choose an S_2 of the form given in Eq. (8) below to guarantee that H_2^+ -diagonal terms remain unchanged:

$$\begin{aligned} S_2 = & S_s^{sss}(1/2)(q_s p_s^3 + p_s^3 q_s) + S_{sss}^s(1/2)(p_s q_s^3 + q_s^3 p_s) \\ & + S_a^{aaa}(1/2)(q_a p_a^3 + p_a^3 q_a) + S_{aaa}^a(1/2)(p_a q_a^3 \\ & + q_a^3 p_a) + S_{aas}^{aas}(1/2)p_a^2(p_s q_s + q_s p_s) \\ & + S_{aas}^{ass}(1/2)p_s^2(p_a q_a + q_a p_a) + S_{aas}^s(1/2)q_a^2(p_s q_s \\ & + q_s p_s) + S_{aas}^a(1/2)q_s^2(p_a q_a + q_a p_a). \end{aligned} \quad (8)$$

The eight coefficients $S_s^{sss} - S_{aas}^a$ can be determined by the condition ${}_n \langle n_s, n_a | H_2^+ | n'_s, n'_a \rangle_n = 0$, if $n'_s, n'_a \neq n_s, n_a$, in the nonresonant case. This condition can be written explicitly in the following way:

$$\begin{aligned} {}_n \langle n_s, n_a | H_2^+ | n'_s, n'_a \rangle_n &= -i {}_n \langle n_s, n_a | [S_2, H_0] | n'_s, n'_a \rangle_n \\ &= -i \hbar c (n_s \omega_s - n_a \omega_a)_n \\ &\quad \times \langle n_s, n_a | S_2 | n'_s, n'_a \rangle_n. \end{aligned} \quad (9)$$

In our model, this relation cannot be applied when $n'_s = n_s \pm 2$ and $n'_a = n_a \pm (-2)$ without incurring the problem of small denominators. The additional requirement $\langle n_s, n_a | [S_2, H_0] | n'_s, n'_a \rangle_n = 0$ for the states $n'_s = n_s \pm 2n'_a = n_a \pm (-2)$ allows one to determine S_2 . This gives rise to a noncompletely diagonal H_2^+ . We report in Appendix A the coefficients of S_2 , and we give all the relations necessary to express all of the coefficients in H^+ and S_2 in terms of just three useful parameters widely used in the literature:²⁴ ω_0 and χ which characterize the Morse-oscillator Hamiltonian of Eq. (A1) [see also Eq. (A2)] equivalent to the quartic potential used here through relations (A3), and λ such that $\omega_a = \omega_0 + \lambda$ and $\omega_s = \omega_0 - \lambda$. We do not report the expression for the matrix $H_0 + H_2^+$, since it is too unwieldy without simplifying approximations. We just say that we have verified that its Taylor expansion in χ and λ , when truncated to first order in χ/ω_0 and λ/ω_0 , is exactly the matrix obtained by the usual perturbative treatment reported by Mills and Robiette,²⁶ apart from a $\chi/4$ additive term in the diagonal introduced later by Lehman.²⁵ These matrices are reported for the first five manifolds also by Halonen,⁶ apart from the zero-point energy. The first-order expansion in χ/ω_0 and λ/ω_0 is equivalent to the usual simplified χ - K relations. The complete matrix H^+ , instead, corresponds to maintaining the more general χ - K relations as reported by Halonen (of course, apart from bending and Coriolis couplings which are reported in Ref. 6). The exact algebraic diagonalization of

${}_n \langle n_s, n_a | H_0 + H_2^+ | n'_s, n'_a \rangle_n$, which we carried out algebraically, gives the resonance-corrected energies and the eigenvectors, which we make to constitute the rows of a unitary matrix U . One may proceed to build the right combination of the transformed eigenvectors $T_1^{-1} \cdot T_2^{-1} | n_s, n_a \rangle_n$ and obtain the wave functions of the whole Hamiltonian H , at second order. The wave functions $\Psi = T_1^{-1} \cdot T_2^{-1} U^{-1} | n_s, n_a \rangle_n$ are essential to calculate the transition moments of the electric and magnetic dipole moment operators and consequently to evaluate the dipole and rotational strengths, as will be done in the next two sections.

We report in Table I, in algebraic form, the eigenvalues and eigenvectors for the matrix ${}_n \langle n_s, n_a | H_0 + H_2^+ | n'_s, n'_a \rangle_n$ truncated at first order in χ and λ for $n_s + n_a = n'_s + n'_a = 0, 1, 2, 3$. The dynamical problem has been examined by many authors,²⁴⁻²⁷ with the aim of proving the equivalence of the normal-mode description versus the local-mode description. The expressions reported in the Table satisfy the relations $|E_{1a} - E_{1b}| > |E_{2a} - E_{2c}| > |E_{3c} - E_{3d}|$ for any value $\chi > 0$ and $\lambda \neq 0$. It is well known²⁴ that when $\lambda < \chi$, the two lowest eigenvalues within each manifold (E_{2a} , E_{2c} and E_{3c} , E_{3d} here) become nearly degenerate with increasing total quantum number, in systems consisting of two identical oscillators.

Consideration of the eigenvectors of Table I at zeroth order in λ and χ gives also the right combinations respecting the symmetry of the two identical CH oscillators. Using the appropriate expressions of the harmonic-oscillator wave functions³⁷ $\phi_i(q_i)$ substituted in $|n_s, n_a\rangle_n = \phi_s(q_s)\phi_a(q_a)$, and considering the coordinate transformation, at zeroth order in ε , from normal coordinates (q_s, q_a) to local coordinates ($\Delta l_I, \Delta l_{II}$) we obtain the following correspondence at zero order:

$$\begin{aligned} \psi_{2a} &= (2)^{-1/2}(|0,2\rangle_n + |2,0\rangle_n) = (2)^{-1/2}(|0,2\rangle_\ell + |2,0\rangle_\ell), \\ \psi_{2b} &= |1,1\rangle_n = (2)^{-1/2}(|0,2\rangle_\ell - |2,0\rangle_\ell), \\ \psi_{3c} &= (1/2)|0,3\rangle_n + (3^{1/2}/2)|2,1\rangle_n \\ &= (2)^{-1/2}(|0,3\rangle_\ell - |3,0\rangle_\ell), \\ \psi_{3d} &= (1/2)|3,0\rangle_n + (3^{1/2}/2)|1,2\rangle_n \\ &= (2)^{-1/2}(|0,3\rangle_\ell + |3,0\rangle_\ell), \end{aligned}$$

$|v_1, v_2\rangle_\ell = \phi_1(\Delta l_I)\phi_2(\Delta l_{II})$ being local-mode harmonic wave functions. This means that the two lowest-energy states in each $(n_s + n_a)$ manifold are local modes, the involvement of both coordinates l_I and l_{II} being required by symmetry.²⁵⁻²⁷ The above relations, providing the local quantum-number-normal-quantum-number correspondence, are correct only at zeroth order in ε since the transformations T_1 and T_2 applied on the Hamiltonian imply coordinates transformations too.

III. DETERMINATION OF DIPOLE TRANSITION MOMENTS

We have modeled the operators of electric dipole moment $\hat{\mu}$ and magnetic dipole moment \hat{m} in a valence-optical approach; accordingly, they are determined only by individual-bond electric dipole moments, which have been

TABLE I. Analytical expressions of eigenvalues and unnormalized eigenvectors of the matrix $\langle n_s, n_a | H_0 + H_2^+ | n'_s, n'_a \rangle$ for $n_s + n_a = n'_s + n'_a = 0, 1, 2, 3$. The matrix was first truncated to first order in λ and χ , and then it was diagonalized. For the notation, see text; the first quantum number refers to the symmetric mode s ; the second one refers to the antisymmetric mode a .

$E_0 = \omega_0 - \frac{1}{2}\chi$	$\Psi_0 = 0,0\rangle$
$E_{1a} = 2\omega_0 - \frac{5}{2}\chi - \lambda$	$\Psi_{1a} = 0,1\rangle$
$E_{1b} = 2\omega_0 - \frac{5}{2}\chi + \lambda$	$\Psi_{1b} = 1,0\rangle$
$E_{2a} = 3\omega_0 - \frac{11}{2}\chi - \sqrt{\chi^2 + 4\lambda^2}$	$\Psi_{2a} = 0,2\rangle + \frac{\sqrt{\chi^2 + 4\lambda^2} - 2\lambda}{\chi} 2,0\rangle$
$E_{2c} = 3\omega_0 - \frac{13}{2}\chi$	$\Psi_{2c} = 1,1\rangle$
$E_{2b} = 3\omega_0 - \frac{11}{2}\chi + \sqrt{\chi^2 + 4\lambda^2}$	$\Psi_{2b} = 0,2\rangle - \frac{\sqrt{\chi^2 + 4\lambda^2} + 2\lambda}{\chi} 2,0\rangle$
$E_{3c} = 4\omega_0 - \frac{21}{2}\chi - \lambda - 2\sqrt{\chi^2 + \lambda^2 - \chi\lambda}$	$\Psi_{3c} = 0,3\rangle - \frac{\sqrt{3}(2\lambda - \chi - 2\sqrt{\chi^2 + \lambda^2 - \chi\lambda})}{3\chi} 2,1\rangle$
$E_{3d} = 4\omega_0 - \frac{21}{2}\chi + \lambda - 2\sqrt{\chi^2 + \lambda^2 + \chi\lambda}$	$\Psi_{3d} = 3,0\rangle - \frac{\sqrt{3}(-2\lambda - \chi - 2\sqrt{\chi^2 + \lambda^2 + \chi\lambda})}{3\chi} 1,2\rangle$
$E_{3a} = 4\omega_0 - \frac{21}{2}\chi - \lambda + 2\sqrt{\chi^2 + \lambda^2 - \chi\lambda}$	$\Psi_{3a} = 0,3\rangle - \frac{\sqrt{3}(2\lambda - \chi + 2\sqrt{\chi^2 + \lambda^2 - \chi\lambda})}{3\chi} 2,1\rangle$
$E_{3b} = 4\omega_0 - \frac{21}{2}\chi + \lambda + 2\sqrt{\chi^2 + \lambda^2 + \chi\lambda}$	$\Psi_{3b} = 3,0\rangle - \frac{\sqrt{3}(-2\lambda - \chi + 2\sqrt{\chi^2 + \lambda^2 + \chi\lambda})}{3\chi} 1,2\rangle$

considered to depend on coordinates and momenta at second order.^{38–41} The electric dipole moment $\vec{\mu}$, in this approximation, is given by $\vec{\mu} = \sum_i \vec{\mu}_i(\Delta\ell_i)$, and for each bond i we assume

$$\vec{\mu}_i(\Delta\ell) = \vec{\mu}_i^0 + \varepsilon \left. \frac{\partial \vec{\mu}_i}{\partial \ell_i} \right|_0 \Delta\ell_i + \varepsilon^2 \left. \frac{\partial^2 \vec{\mu}_i}{\partial \ell_i^2} \right|_0 \Delta\ell_i^2, \quad (10)$$

with no contributions from cross-terms $\left. \frac{\partial \vec{\mu}_i}{\partial \ell_j} \right|_0$ with $i \neq j$. This simplifying assumption easily allows one to use electro-optical parameters derived from absorption overtone spectroscopy,^{34,35} but may be eventually dropped if one wants to use the parameters of more advanced calculations. As is usual in overtone spectroscopy, in our HCCH fragment we consider just the CH bond dipole moments and we ignore the CC bond contribution: then, the index i runs from I to II (we use Roman numbers for bonds and Arabic numbers for orders of approximation). In order to apply the perturbative approach illustrated above we need to work in normal coordinates, the dipole moment being

$$\begin{aligned} \vec{\mu} &= \vec{\mu}^0 + \varepsilon \sum_{\alpha} \vec{\mu}_{\alpha} q_{\alpha} + \varepsilon^2 \frac{1}{2} \sum_{\alpha, \beta} \vec{\mu}_{\alpha\beta} q_{\alpha} \cdot q_{\beta} \\ &= \vec{\mu}_0 + \varepsilon \vec{\mu}_1 + \varepsilon^2 \vec{\mu}_2. \end{aligned} \quad (11)$$

Considering the general relation between normal and local coordinates, one obtains^{37,38}

$$\vec{\mu}_{\alpha} = \left. \frac{\partial \vec{\mu}}{\partial q_{\alpha}} \right|_0 = \sum_i \frac{\partial \vec{\mu}_i}{\partial \ell_i} \left(\sum_A \vec{s}_{iA} \cdot \vec{t}_{A\alpha} \right), \quad (12)$$

\vec{s}_{iA} being the Wilson³⁷ vector relating internal coordinates to Cartesian displacements and $\vec{t}_{A\alpha}$ being given in Appendix A.

Referring to the molecular fragment of Fig. 1, the transformations relating CH-stretching internal coordinates to dimensionless normal ones are simply

$$q_a = \alpha_a \sqrt{m/2} (\Delta\ell_I - \Delta\ell_{II}), \quad q_s = \alpha_s \sqrt{m/2} (\Delta\ell_I + \Delta\ell_{II}),$$

where α_i are the coefficients allowing one to go from the usual normal coordinates to mass-weighted ones, reported in Eq. (A4) of Appendix A, and m is the reduced mass of the CH bond. Since $\left. \frac{\partial \vec{\mu}_i}{\partial \ell_i} \right|_0$ are identical in magnitude for the two CH bonds, due to the C_2 symmetry, and since they are assumed to be directed along the bonds, i.e., $\left. \frac{\partial \vec{\mu}_i}{\partial \ell_i} \right|_0 = \frac{\partial \mu}{\partial \ell} \big|_0 \hat{\mathbf{u}}_i$ ($\hat{\mathbf{u}}_i$ being the unit vector of bond i , $i = I, II$), the coefficients of Eq. (11) as functions of valence optical parameters $\left. \frac{\partial \mu}{\partial \ell} \right|_0$ and $\left. \frac{\partial^2 \mu}{\partial \ell^2} \right|_0$ are

$$\vec{\mu}_{\alpha} = \left. \frac{\partial \vec{\mu}}{\partial q_{\alpha}} \right|_0 = \frac{\partial \mu}{\partial \ell} \bigg|_0 \frac{\hat{\mathbf{u}}_I \pm \hat{\mathbf{u}}_{II}}{\sqrt{2m\alpha_{\alpha}}} \quad (+ \text{ if } \alpha = s, - \text{ if } \alpha = a) \quad (13)$$

and

$$\vec{\mu}_{\alpha\alpha} = \frac{\partial^2 \vec{\mu}}{\partial q_\alpha^2} \Big|_0 = \frac{\partial^2 \mu}{\partial \ell^2} \Big|_0 \frac{\hat{\mathbf{u}}_I + \hat{\mathbf{u}}_{II}}{2m\alpha_\alpha^2} \quad (\alpha = s, a), \quad (14)$$

$$\begin{aligned} \vec{\mu}_{\alpha\beta} &= \frac{\partial^2 \vec{\mu}}{\partial q_\alpha \partial q_\beta} \Big|_0 \\ &= \frac{\partial^2 \mu}{\partial \ell^2} \Big|_0 \frac{\hat{\mathbf{u}}_I - \hat{\mathbf{u}}_{II}}{2m\alpha_\alpha\alpha_\beta}, \quad \alpha \text{ different from } \beta. \end{aligned} \quad (15)$$

For the total magnetic dipole moment $\vec{\mathbf{m}}$, we adopt the bond dipole valence optical approach, as described in Refs. 39 and 40:

$$\vec{\mathbf{m}} = \frac{1}{2c} \sum_i (\vec{\mathbf{r}}_{Ai} \times \dot{\vec{\mu}}_i + \vec{\mu}_i \times \dot{\vec{\mathbf{r}}}_{Bi}), \quad (16)$$

where A_i and B_i are the two atoms defining bond i . Referring to the chiral fragment of Fig. 1, let us take the coordinate origin in C_1 ; in the hypothesis that r_{CII} is fixed and that $\hat{\mathbf{u}}_i$ and $\dot{\vec{\mu}}_i$ are always parallel to the fixed direction $\hat{\mathbf{u}}_i$ given by the equilibrium orientation of bond i , one obtains

$$\vec{\mathbf{m}} = \frac{1}{2c} \vec{\mathbf{r}}_{CII} \times \dot{\vec{\mu}}_{II}. \quad (16')$$

Analogously to the electric dipole moment, we need an expression of $\vec{\mathbf{m}}$ as a function of normal coordinates and/or conjugated momenta:

$$\begin{aligned} \vec{\mathbf{m}} &= \vec{\mathbf{m}}_0 + \varepsilon \sum_\alpha \vec{\xi}^\alpha p_\alpha + \varepsilon^2 \sum_{\alpha,\beta} \vec{\xi}^\beta \left(\frac{q_\alpha \cdot p_\beta + p_\beta \cdot q_\alpha}{2} \right) \\ &= \vec{\mathbf{m}}_0 + \varepsilon \cdot \vec{\mathbf{m}}_1 + \varepsilon^2 \vec{\mathbf{m}}_2. \end{aligned} \quad (17)$$

Since $\dot{q}_\alpha = \alpha_\alpha^2 \cdot p_\alpha$ (see Appendix A),

$$\begin{aligned} \vec{\xi}^\alpha &= \frac{1}{2c} \vec{\mathbf{r}}_{CII} \times \frac{\partial \vec{\mu}_{II}}{\partial \ell_{II}} \left(\sum_A \vec{s}_{2A} \cdot \vec{\mathbf{t}}_{A\alpha} \right) \cdot \alpha_\alpha^2 \\ &= \pm \frac{1}{2c} \vec{\mathbf{r}}_{CII} \times \left(\frac{\partial \mu}{\partial \ell} \right) \frac{\alpha_\alpha}{\sqrt{2m}} \hat{\mathbf{u}}_{II}, \quad + \text{ if } \alpha = s, - \text{ if } \alpha = a, \end{aligned} \quad (18)$$

$$\vec{\xi}^\beta = \pm \frac{1}{2c} \vec{\mathbf{r}}_{CII} \times \left(\frac{\partial^2 \mu}{\partial \ell^2} \right) \frac{\alpha_\beta}{2m\alpha_\alpha} \hat{\mathbf{u}}_{II}, \quad + \text{ if } \alpha = \beta, - \text{ if } \alpha \neq \beta. \quad (19)$$

The rotational strength

$$\mathcal{R} = \text{Im} \langle {}_n \langle \Psi_0 | \vec{\mu} | \Psi_f \rangle_n \cdot {}_n \langle \Psi_f | \vec{\mathbf{m}} | \Psi_0 \rangle_n \rangle \quad (20)$$

has been demonstrated to be origin independent for the fundamental transition $0 \rightarrow 1$.³⁹ The same invariance needs to be proved for the overtone and combination transitions. Dipole strengths and rotational strengths are obtained from the transition moments evaluated on the perturbed wave functions $\Psi = T_1^{-1} T_2^{-2} U^{-1} |n_s, n_a\rangle_n$. Alternatively, one may apply Van Vleck contact transformations directly on operators; we can easily construct $\hat{\mu}^+$ and $\hat{\mathbf{m}}^+$ from Eqs. (2) and (6), with the help of the algebraic manipulator code:

$$\begin{aligned} \hat{\mu}^+ &= T_2 \cdot T_1 \cdot \hat{\mu} \cdot T_1^{-1} \cdot T_2^{-1} \\ &= \hat{\mu}_0^+ + \varepsilon \hat{\mu}_1^+ + \varepsilon^2 \hat{\mu}_2^+ + \varepsilon^3 \hat{\mu}_3^+ + \varepsilon^4 \hat{\mu}_4^+, \end{aligned}$$

$$\begin{aligned} \hat{\mathbf{m}}^+ &= T_2 \cdot T_1 \cdot \hat{\mathbf{m}} \cdot T_1^{-1} \cdot T_2^{-1} \\ &= \hat{\mathbf{m}}_0^+ + \varepsilon \hat{\mathbf{m}}_1^+ + \varepsilon^2 \hat{\mathbf{m}}_2^+ + \varepsilon^3 \hat{\mathbf{m}}_3^+ + \varepsilon^4 \hat{\mathbf{m}}_4^+. \end{aligned}$$

Considering homologous terms in ε and being the initial operators μ and \mathbf{m} in Eqs. (11) and (17) of the form $\hat{f} = \hat{f}_0 + \varepsilon \cdot \hat{f}_1 + \varepsilon^2 \cdot \hat{f}_2$, with f_0 independent of p and q , the transformations (2) and (6) can be written

$$\begin{aligned} \hat{f}_0^+ &= \hat{f}_0, \\ \hat{f}_1^+ &= \hat{f}_1, \\ \hat{f}_2^+ &= \hat{f}_2 + i[S_1, \hat{f}_1], \\ \hat{f}_3^+ &= i[S_1, \hat{f}_2] - \frac{1}{2}[S_1, [S_1, \hat{f}_1]] + i[S_2, \hat{f}_1], \\ \hat{f}_4^+ &= -\frac{1}{2}[S_1, [S_1, \hat{f}_2]] - \frac{i}{6}[S_1, [S_1, [S_1, \hat{f}_1]]] \\ &\quad + i[S_2, \hat{f}_2] - [S_2, [S_1, \hat{f}_1]]. \end{aligned} \quad (21)$$

In the calculations presented in the next paragraph we keep terms up to fourth order. The expressions of the transformed operators, as functions of the electric and magnetic dipole moment coefficients $\vec{\mu}_\alpha$, $\vec{\mu}_{\alpha\beta}$, ξ^α , ξ_α^β and of the transformation coefficients S_{ijk} and S_{ijkl} , are very long. We report them in Appendix B, Eqs. (B1)–(B6), truncated at third order. In Appendix C we report the proof of the origin independence of the rotational strengths obtained with the transformed operators $\hat{\mu}^+$ and $\hat{\mathbf{m}}^+$, for the first two overtone transitions. With the aid of the algebraic manipulator used to build $\hat{\mu}^+$ and $\hat{\mathbf{m}}^+$, one can easily substitute numerical values for $\partial\mu/\partial\ell|_0$ and $\partial^2\mu/\partial\ell^2|_0$ and ω_0 , χ , and λ , and one can calculate numerically dipole and rotational strengths for HCCH fragments with different dynamical and electrical characteristics. Before considering the specific numerical example treated in the following paragraph, a few comments on the analytical findings are worthwhile.

The transition moments based on harmonic uncoupled-oscillator wave functions $|n_s, n_a\rangle_n$ depend on the electrooptical parameters μ_α , $\mu_{\alpha\beta}$, ξ_α , ξ_α^β and on the S_{ijk} and S_{ijkl} coefficients. Of course, first-order terms in ε contribute only to $0 \rightarrow 1$ transitions by linear electrical coefficients (with minor corrections from all successive odd-order terms), ε^2 terms contribute only to $0 \rightarrow 2$ transitions by linear electrical terms multiplied by S_{ijk} , and quadratic electrical terms (and minor corrections from successive even-order terms). The $0 \rightarrow 3$ transitions have contributions from ε^3 terms, linear electrical terms are multiplied by S_{ijkl} or by $S_{ijk} \cdot S_{i'j'k'}$, and quadratic terms are multiplied by S_{ijk} . The $0 \rightarrow 4$ transitions derive from ε^4 terms. From Appendix A we know that in the approximation $\omega_s \approx \omega_a \approx \omega_0$ the coefficients of the generating functions are of the following orders of magnitude:

$$S_{ijk} \cong \sqrt{\chi/\omega_0}, \quad S_{ijkl} \cong \chi/\omega_0.$$

TABLE II. Final states ψ_f at zero order in χ and λ , approximate transition frequencies $\omega_f - \omega_i$ in the hypothesis $\lambda \ll \chi$, and principal terms in $\sqrt{\chi/\omega}$ of dipole strengths \mathcal{D} and rotational strengths \mathcal{R} from the ground state $|0,0\rangle$ towards the final states ψ_f for $n_s + n_a = 1, 2, 3$. For the definition of symbols used, see text.

ψ_f	$\omega_f - \omega_i$	\mathcal{D}	\mathcal{R}
$ 0,1\rangle$	$\omega_0 - 2\chi - \lambda$	$\frac{\vec{\mu}_a^2}{2} + \dots$	$\frac{\hbar}{2} \vec{\mu}_a \cdot \vec{\xi}_a + \dots$
$ 1,0\rangle$	$\omega_0 - 2\chi + \lambda$	$\frac{\vec{\mu}_s^2}{2} + \dots$	$\frac{\hbar}{2} \vec{\mu}_s \cdot \vec{\xi}_s + \dots$
$\frac{1}{\sqrt{2}}(0,2\rangle + 2,0\rangle)$	$2\omega_0 - 6\chi - \frac{2\lambda^2}{\chi}$	$\frac{1}{16} \left(\vec{\mu}_{aa} + \vec{\mu}_{ss} - 2\sqrt{\frac{\chi}{\omega}} \vec{\mu}_s \right)^2 + \dots$	$\frac{\hbar}{8} \left(\vec{\mu}_{aa} + \vec{\mu}_{ss} - 2\sqrt{\frac{\chi}{\omega}} \vec{\mu}_s \right) \cdot \left(\vec{\xi}_{aa} + \vec{\xi}_{ss} - 2\sqrt{\frac{\chi}{\omega}} \vec{\xi}_s \right) + \dots$
$ 1,1\rangle$	$2\omega_0 - 6\chi$	$\frac{1}{4} \left(\vec{\mu}_{sa} - \sqrt{\frac{\chi}{\omega}} \vec{\mu}_a \right)^2 + \dots$	$\frac{\hbar}{4} \left(\vec{\mu}_{sa} - \sqrt{\frac{\chi}{\omega}} \vec{\mu}_a \right) \cdot \left(\vec{\xi}_s^a + \vec{\xi}_a - 2\sqrt{\frac{\chi}{\omega}} \vec{\xi}_a \right) + \dots$
$\frac{1}{\sqrt{2}}(0,2\rangle - 2,0\rangle)$	$2\omega_0 - 4\chi + \frac{2\lambda^2}{\chi}$	$\frac{1}{16} (\vec{\mu}_{aa} - \vec{\mu}_{ss})^2 + \dots$	$\frac{\hbar}{8} (\vec{\mu}_{aa} - \vec{\mu}_{ss}) \cdot (\vec{\xi}_{aa} - \vec{\xi}_{ss}) + \dots$
$\frac{1}{2} 0,3\rangle + \frac{\sqrt{3}}{2} 2,1\rangle$	$3\omega_0 - 12\chi - \frac{3\lambda^2}{4\chi}$	$\frac{3}{4} \frac{\chi}{\omega} \left(\vec{\mu}_{sa} - \frac{2}{3} \sqrt{\frac{\chi}{\omega}} \vec{\mu}_a \right)^2 + \dots$	$\hbar \frac{3}{4} \frac{\chi}{\omega} \left(\vec{\mu}_{sa} - \frac{2}{3} \sqrt{\frac{\chi}{\omega}} \vec{\mu}_a \right) \cdot \left(\frac{3}{2} (\vec{\xi}_s^a + \vec{\xi}_a) - 2\sqrt{\frac{\chi}{\omega}} \vec{\xi}_a \right) + \dots$
$\frac{1}{2} 3,0\rangle + \frac{\sqrt{3}}{2} 1,2\rangle$	$3\omega_0 - 12\chi - \frac{3\lambda^2}{4\chi}$	$\frac{3}{4} \frac{\chi}{\omega} \left[\frac{1}{2} (\vec{\mu}_{ss} + \vec{\mu}_{aa}) - \frac{2}{3} \sqrt{\frac{\chi}{\omega}} \vec{\mu}_s \right]^2 + \dots$	$\hbar \frac{3}{4} \frac{\chi}{\omega} \left(\frac{1}{2} (\vec{\mu}_{ss} + \vec{\mu}_{aa}) - \frac{2}{3} \sqrt{\frac{\chi}{\omega}} \vec{\mu}_s \right) \cdot \left(\frac{3}{2} \vec{\xi}_{aa} - 2\sqrt{\frac{\chi}{\omega}} \vec{\xi}_s \right) + \dots$
$\frac{\sqrt{3}}{2} 0,3\rangle - \frac{1}{2} 2,1\rangle$	$3\omega_0 - 8\chi - 2\lambda + \frac{3\lambda^2}{4\chi}$	0	0
$\frac{\sqrt{3}}{2} 3,0\rangle - \frac{1}{2} 1,2\rangle$	$3\omega_0 - 8\chi + 2\lambda + \frac{3\lambda^2}{4\chi}$	$\frac{1}{16} \frac{\chi}{\omega} (\vec{\mu}_{aa} - \vec{\mu}_{ss})^2 + \dots$	$\hbar \frac{3}{16} \frac{\chi}{\omega} (\vec{\mu}_{aa} - \vec{\mu}_{ss}) \cdot (\vec{\xi}_{aa} - 2\vec{\xi}_{ss}) + \dots$

In Table II we report the leading term in $\sqrt{\chi/\omega}$ for dipole and rotational strengths. These approximate analytical expressions give an estimate of absorption and VCD spectra for the fundamental transitions ($n = n_s + n_a = 1$), as well as for the first two overtone regions ($n = 2, 3$). The limitations of these approximations will be tested in the numerical example given in the next section. A few observations can be made based on the results of Table II. As long as electrical anharmonicity can be ignored, as, e.g., in the fixed partial charge approximation,³⁸ the dipole strengths for the first overtone region ($n_s + n_a = 2$) are smaller than those for the fundamental region by a factor of χ/ω and those for the second overtone region ($n_s + n_a = 3$) by a factor of $(\chi/\omega)^2$. As a consequence, a decrease in intensity of nearly two orders of magnitude at each overtone order (with reasonable CH stretching parameter values as those used in the next section) is to be expected. This rapid decrease is indeed observed only from fundamentals to first overtones; for successive overtones, there is a less marked decrease and this has been attributed to the fact that electrical anharmonicity is important.³⁴⁻³⁶ A further consequence of the hypothesis of zero electrical anharmonicity is that the two transitions at lowest frequency within each manifold are the only ones predicted to be observable: moreover, they have nearly equal absorption intensity and opposite rotational strengths. Dealing with the $\Delta n = 3$ region, one sees from Table II that the two lowest-lying transitions are so close as to make any observation of rotational strength impossible.

In conclusion, the presence of electrical anharmonicity is necessary to ensure the right decrease of intensities among different manifolds and confirms the predominance of the two low-frequency transitions within the same manifold.

Rough estimates of the intensity parameters are obtained introducing the quantity $\gamma = (1/2\pi) \sqrt{\hbar N_A / 2c \omega_0}$ ($\gamma \approx 0.075 \text{ \AA}$ when $\omega_0 = 3000 \text{ cm}^{-1}$). We have

$$\mu_\alpha \approx \gamma \frac{\partial \mu}{\partial \ell} \Big|_0, \quad \xi_\alpha^\alpha \approx \hbar^{-1} \pi r_{CC} \gamma \frac{\partial \mu}{\partial \ell} \Big|_0 \omega_0,$$

$$\mu_{\beta\alpha} \approx \gamma^2 \frac{\partial^2 \mu}{\partial \ell^2} \Big|_0, \quad \xi_\alpha^\beta \approx \hbar^{-1} \pi r_{CC} \gamma^2 \frac{\partial^2 \mu}{\partial \ell^2} \Big|_0 \omega_0.$$

Regardless of the electro-optical parameters adopted, $\partial \mu / \partial \ell|_0$ and $\partial^2 \mu / \partial \ell^2|_0$, and taking $r_{CC} = 1.54 \text{ \AA}$, $\omega_0 = 3000 \text{ cm}^{-1}$, one has $\mathcal{R}_{0 \rightarrow v} = 1.4 \times 10^{-4} \cdot \mathcal{D}_{0 \rightarrow v}$. This gives a dissymmetry factor $G = 4\mathcal{R}/\mathcal{D} = 4\pi r_{CC} \omega_0 \approx 6 \times 10^{-4}$ independently of v , as experimentally observed thus far in most cases.^{3,42}

Let us make a final comment regarding the number of transformations needed in the Van Vleck procedure. The Hamiltonian of Eq. (1) has been diagonalized to second order in ε , and the use of zeroth order eigenfunctions is justified since the corrections are taken into account on the operators. In general the transformed Hamiltonian

$$H^+ = H_0^+ + \varepsilon \cdot H_1^+ + \varepsilon^2 \cdot H_2^+ + \varepsilon^3 \cdot H_3^+ + \varepsilon^4 \cdot H_4^+ + \dots$$

TABLE III. Values for the mechanical CH bond parameters ω_0, χ, λ and for the electric bond dipole moment parameters $\partial\mu/\partial\ell|_0, \partial^2\mu/\partial\ell^2|_0$ employed in the numerical example of Table IV (for the latter parameters see Ref. 31). We also report the corresponding normal-mode parameters derived as described in Appendix A.

$\omega_0 = 3000 \text{ cm}^{-1}$			
$\chi = 60 \text{ cm}^{-1}$			$\partial\mu/\partial\ell _0 = -0.143e$
$\lambda = 20 \text{ cm}^{-1}$			$\partial^2\mu/\partial\ell^2 _0 = -0.485e/\text{\AA}$
Parameters derived from the preceding ones			
ω_s	3020 cm^{-1}		
ω_a	2980 cm^{-1}	$ \mu_s = 0.872 \times 10^{-19} \text{ esu cm}$	$\hbar \xi_s = 0.706 \times 10^{-23} \text{ esu cm}$
K_{sss}	-210.1 cm^{-1}	$ \mu_a = 0.620 \times 10^{-19} \text{ esu cm}$	$\hbar \xi_a = 0.702 \times 10^{-23} \text{ esu cm}$
K_{saa}	-638.7 cm^{-1}	$ \mu_{ss} = 0.110 \times 10^{-21} \text{ esu cm}$	$\hbar \xi_a^s = 0.865 \times 10^{-26} \text{ esu cm}$
K_{ssss}	17.3 cm^{-1}	$ \mu_{aa} = 0.112 \times 10^{-21} \text{ esu cm}$	$\hbar \xi_s^a = 0.854 \times 10^{-26} \text{ esu cm}$
K_{aaaa}	17.7 cm^{-1}	$ \mu_{sa} = 0.785 \times 10^{-22} \text{ esu cm}$	$\hbar \xi_{aa} = 0.859 \times 10^{-26} \text{ esu cm}$
K_{ssaa}	105 cm^{-1}		$\hbar \xi_{ss} = 0.859 \times 10^{-26} \text{ esu cm}$

contains terms in $\varepsilon^3, \varepsilon^4, \dots$ which are not diagonal and can be diagonalized by introducing further contact transformations generated by S_3, S_4, \dots . These generating functions give rise to further corrections on the operators $\hat{\mu}$ and \hat{m} . Our treatment has been coherently developed up to third order in ε for $\hat{\mu}$ and \hat{m} . Indeed, from Eq. (21) one observes that S_1 gives origin to corrections in ε^2 and S_2 to corrections in ε^3 . If one imagines to carry on the perturbative treatment with a function S_3 , the third-order term will not be corrected anymore ($\mu_3^{++} = \mu_3^+$), while the fourth-order term will become $\mu_4^{++} = \mu_4^+ + i[S_3, \mu_1]$. This is the reason why our treatment can be considered satisfactory for the $\Delta v = 1, 2, 3$ transitions and needs to be improved for $\Delta v \geq 4$. Since the contribution of electrical anharmonicity (μ_2 term) is greater than the μ_1 term,³⁵ we expect our results to be quite acceptable also for $\Delta v = 4$ in the numerical case we examined, even without making the transformation S_3 ; of course, this would not be the case with $\partial^2\hat{\mu}/\partial\ell^2|_0 \approx 0$. The analytical expressions for $\Delta v = 4$ do not allow any further insight into the description of the normal-mode to local-mode transition, and we do not report them here.

IV. NUMERICAL EXAMPLE

In this section we present a numerical example where we have used the complete expressions of operators $\hat{\mu}$ and \hat{m} to fourth order in order to calculate intensities and rotational strengths for a case representing aliphatic CH's. The operators, due to all the relations given in Appendix A, ultimately depend only on the mechanical parameters ω_0, χ , and λ and on the electrical parameters $\partial\mu/\partial\ell|_0$ and $\partial^2\mu/\partial\ell^2|_0$. The values for those parameters used in the calculation are given in Table III. Here ω_0 and χ values refer to no specific molecule but are well representative of aliphatic CH's. Also, $\partial\mu/\partial\ell|_0$ and $\partial^2\mu/\partial\ell^2|_0$ have been taken from a previous work by our group on overtone absorption intensities,³⁵ where overtone experimental absorption intensity data were used to parametrize the bond electric dipole moment, expressed through a linear plus a quadratic dependence on the bond stretching coordinate. In that work, as in many other well-known papers³⁴⁻³⁶ in the literature, the importance of electrical anharmonicity had been pointed out, and different functional dependences have also been proposed. In Table III

TABLE IV. Final states, transition frequencies ω , dipole strengths \mathcal{D} , and rotational strengths \mathcal{R} calculated for the fundamental and first three overtones in the numerical case defined by the parameters reported in Table III on the basis of the perturbative treatment, with no further approximation (columns 1-4). In columns 5 and 6 the corresponding approximated values for the fundamental and first two overtones have been obtained according to the results of Table II.

Final state $U^{-1} n_s, n_a\rangle$	$\omega \text{ (cm}^{-1}\text{)}$	$\mathcal{D} \text{ (esu}^2\text{ cm}^2\text{)}$	$\mathcal{R} \text{ (esu}^2\text{ cm}^2\text{)}$	$\mathcal{D} \text{ (esu}^2\text{ cm}^2\text{)}$	$\mathcal{R} \text{ (esu}^2\text{ cm}^2\text{)}$
(0,1)	2862	0.23×10^{-38}	-0.19×10^{-42}	0.19×10^{-38}	-0.16×10^{-42}
(1,0)	2903	0.46×10^{-38}	0.19×10^{-42}	0.38×10^{-38}	0.16×10^{-42}
0.88(0,2)+0.47(2,0)	5632	0.29×10^{-40}	0.18×10^{-44}	0.37×10^{-40}	0.31×10^{-44}
(1,1)	5644	0.16×10^{-40}	-0.21×10^{-44}	0.19×10^{-40}	-0.31×10^{-44}
0.47(0,2)-0.88(2,0)	5780	0.29×10^{-41}	0.20×10^{-45}	0.14×10^{-48}	0
0.64(0,3)+0.77(2,1)	8280	0.16×10^{-41}	-0.41×10^{-45}	0.50×10^{-42}	-0.12×10^{-45}
0.39(3,0)+0.92(1,2)	8281	0.33×10^{-41}	0.41×10^{-45}	0.99×10^{-42}	0.12×10^{-45}
0.64(2,1)-0.77(0,3)	8497	0.37×10^{-43}	-0.96×10^{-47}	0	0
0.92(3,0)-0.39(1,2)	8579	0.42×10^{-43}	0.55×10^{-47}	0.27×10^{-50}	-0.26×10^{-52}
0.44(0,4)+0.28(4,0)+0.85(2,2)	10802	0.25×10^{-42}	-0.52×10^{-46}		
0.62(3,1)+0.78(1,3)	10802	0.14×10^{-42}	0.55×10^{-46}		
0.41(4,0)-0.86(0,4)+0.31(2,2)	11149	0.21×10^{-44}	-0.46×10^{-48}		
0.62(1,3)-0.78(3,1)	11182	0.18×10^{-44}	0.58×10^{-48}		
0.26(0,4)+0.87(4,0)-0.42(2,2)	11336	0.20×10^{-45}	-0.44×10^{-49}		

we also give the corresponding values of the normal-mode anharmonic force constants K_{ijl} , K_{ijkl} and of the normal-mode electric and magnetic dipole moment coefficients μ_α , $\mu_{\alpha\beta}$, ξ_α , ξ_α^β , according to the relations in Appendix A and to Eqs. (13)–(15) and (18), (19). In Table IV we report the results for frequencies, dipole strengths, and rotational strengths of the transitions from the ground state to eigenstates of the fourth-order Hamiltonian H^+ up to the third overtone, with inclusion of the DD resonance, that is to say, the states $\mathbf{U}^{-1}|n_s, n_a\rangle_n$ (with $n_s + n_a = 4$). In Table IV we also compare the numerical results obtained by running the perturbative treatment to the best of the present approximation with the results obtained with the approximate analytical derivations of Table II: the approximate formulas give the correct orders of magnitude only for the two most intense transitions at each overtone order. This is due to the approximation $\omega_s \cong \omega_a$, which is not acceptable for the other transitions.

The results presented in Table IV are quite satisfactory. First of all, the decrease of overtone absorption intensities by two orders of magnitude in going from fundamentals to first overtones and by one order of magnitude at each successive overtone has been observed also in CD for some terpenes and cyclic ketones.³ These observations are matched by our numerical results of Table IV for $\Delta n = 1, 2, 3, 4$. The electrical parameters are such that $\partial^2 \mu / \partial \ell^2|_0$ starts to contribute at $\Delta n = 2$, and at this overtone order its contribution is in part canceled by the contribution of the linear term, thus explaining the more rapid decrease of the first overtone with respect to the others.

Furthermore, we observe that the highest absorption intensities within each manifold are due to two nearly degenerate vibrations at very low frequency (not yet degenerate at $\Delta n = 2$). As can also be seen from Tables I and II for $\Delta n = 2$, $\Delta n = 3$, both these two states are linear symmetric combinations of states $|n_s, n_a\rangle_n$ coupled via DD interactions. All other vibrational states correspond to dipole strengths at least one order of magnitude lower. From our calculations we see that the same happens for rotational strengths, but at each overtone order the two degenerate states have opposite signs and so they tend to cancel one another.

The results obtained here for dipole strengths are exactly as expected in the local mode picture: considering the two CH bonds as “local” anharmonic oscillators of quantum states $|v_I, v_{II}\rangle_\ell$,^{28,34} both from classical and quantum studies, one obtains that overtones $|v, 0\rangle_\ell$ (with $v = v_I + v_{II}$) have lower frequencies and higher intensities than combination states, so that the bands usually observed in near-infrared (NIR) spectroscopy (in absence of Fermi resonances) are due to nearly degenerate states $|v, 0\rangle_\ell \pm |0, v\rangle_\ell$. If one considers these states in Eq. (20) as defining rotational strengths, in the valence bond approach of Eqs. (10) and (16), one has

$$\begin{aligned} \mathcal{R} &= \text{Im}(\langle 0, 0 | \vec{\mu}_I | (v, 0) \pm (0, v) \rangle_\ell \cdot \langle (v, 0) \pm (0, v) | \vec{\mathbf{m}}_{II} | 0, 0 \rangle_\ell) \\ &= \pm \text{Im} \left(\langle 0, 0 | \vec{\mu}_I | v, 0 \rangle_\ell \cdot \frac{r_{CC}}{2c} \times \langle v, 0 | \dot{\vec{\mu}}_{II} | 0, 0 \rangle_\ell \right), \end{aligned}$$

thus giving origin to rotational strengths of opposite signs.

V. CONCLUSIONS

In this work we have presented the analytical expressions of frequencies, dipole strengths, and rotational strengths for the fundamental CH-stretching region and the first two overtone regions in a HCCH chiral fragment with C_2 symmetry. This work has been made possible by the use of the Van Vleck contact transformation scheme performed by means of an algebraically based computer code. The expressions obtained for the transformed operators in Appendix B and for approximate dipole and rotational strengths in Table II are valid for the most general dipole with quadratic dependence [see Eqs. (11) and (17)]; they do not require a valence bond optical model. It is only the evaluation of the coefficients of Eqs. (11) and (17) that is based on the coupled-oscillator valence optical hypothesis. Our final numerical calculations rely on the assumption of bond-localized mechanical and electrical properties. Despite the approximations made, the analytical dependences on the parameters allow one to gain a deep insight into the normal-mode to local-mode transition and the spectroscopic signature of it. The role of each parameter is well evidenced by the present treatment. As already well known, it is the DD coupling that is essential in generating the eigenstates that reproduce the usually observed local modes at high Δv 's. From the expressions obtained for dipole strengths the role of the electrical anharmonicity and the prevalence of low-frequency modes in absorption are well documented. The novelty of this work, however, mostly regards rotational strengths of overtone transitions. The numerical results given in Table IV can be considered to represent well both fundamental and overtone data for a transition from a normal-mode regime to a local-mode one. For this reason a treatment like the one undertaken here is beyond the two crude simplifying starting schemes—that is to say, the normal-mode approach and the local-mode approach. If the two bonds are mechanically identical as imposed here, they give origin to degenerate local modes with rotational strengths of opposite signs. Of course, the prediction that no VCD beyond $\Delta v = 2$ can be observed for an HCCH fragment of the sort examined here, with two identical oscillators, is in some cases against experimental evidence.³ At this point the following assumptions need to be revised in the model: (i) the two CH bonds are equivalent, (ii) coupling to other modes such as torsion⁴ is negligible, and (iii) molecular electric and magnetic dipole moments are generated by bond electric dipole moments. Anyway, the procedure of Van Vleck transformations adopted here is quite promising also in view of overcoming these limitations: it can be extended to a higher number of oscillators¹⁹ and, what is more important for CD, it can be applied to operators μ and \mathbf{m} with the general form of Eqs. (11) and (17) without the too severe hypothesis of valence bond optical approach. In fact, our experimental findings propose both conservative bisignate spectra compatible with coupled bond dipoles, as described here, and nonconservative monosignate spectra,³ which require a different model for the magnetic moment operator, as already recognized and amply done to interpret VCD spectra in the infrared.^{17,43}

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APPENDIX A: DEPENDENCE OF S_1 AND S_2 COEFFICIENTS ON ANHARMONIC FORCE CONSTANTS

We wish to recall here the dependences of the anharmonic force constants K_{sss} , K_{saa} , K_{ssss} , K_{aaaa} , and K_{ssaa} of Hamiltonian (1) in the text, considering it as the fourth-order approximation of two harmonically coupled symmetry-equivalent Morse oscillators representing two equivalent bonds and transformed from bond (local) coordinates to normal coordinates, i.e.,

$$H = (p_1^2/2m) + (p_{II}^2/2m) + D[1 - \exp\{-a(l_I - l_0)\}]^2 + D[1 - \exp\{-a(l_{II} - l_0)\}]^2 + K_{I,II}(l_I - l_0)(l_{II} - l_0). \quad (A1)$$

We recall the relations between Morse parameters D and a to the mechanical frequency ω_0 and anharmonicity χ :^{4,24}

$$D = \omega_0^2/4\chi, \quad a = \sqrt{8\pi^2 mc\chi/h}. \quad (A2)$$

The third and fourth derivatives of the Morse potential evaluated at equilibrium are

$$K_{III} = (\partial^3 V/\partial l^3) = -6a^3 D, \quad K_{IIII} = (\partial^4 V/\partial l^4) = 14a^4 D. \quad (A3)$$

The Hamiltonian used in the perturbative treatment is obtained by diagonalizing the zeroth-order term, i.e., considering normal modes. The frequencies of the two normal oscillators are

$$\omega_s = \omega_0 + \lambda, \quad \omega_a = \omega_0 - \lambda,$$

where $\lambda = \frac{1}{2}K_{I,II}/4\pi^2 c^2 m \omega_0$, with m the reduced mass of the CH bond. Dimensionless normal coordinates q_α are related to the usual ones Q_α by $q_\alpha = \alpha_\alpha Q_\alpha$, where

$$\alpha_\alpha = [2\pi c \omega_\alpha / \hbar]^{1/2} \quad (\alpha = s, a). \quad (A4)$$

The Hamiltonian used in the perturbative treatment is that of Eq. (1) with coefficients given by

$$K_{sss} = (6\sqrt{2}m^{3/2}hc)^{-1} \alpha_s^{-3} K_{III}, \quad (A5a)$$

$$K_{saa} = (2\sqrt{2}m^{3/2}hc)^{-1} \alpha_s^{-1} \alpha_a^{-2} K_{III}, \quad (A5b)$$

$$K_{ssss} = (48m^2 hc)^{-1} \alpha_s^{-4} K_{IIII}, \quad (A5c)$$

$$K_{aaaa} = (48m^2 hc)^{-1} \alpha_a^{-4} K_{IIII}, \quad (A5d)$$

$$K_{ssaa} = (8m^2 hc)^{-1} \alpha_s^{-2} \alpha_a^{-2} K_{IIII}. \quad (A5e)$$

Inserting Eqs. (A3) into Eqs. (A5) and making use of Eq. (A2), one obtains

$$K_{sss} = -\frac{\sqrt{\chi}\omega_0^2}{2\omega_s^{3/2}}, \quad K_{saa} = -\frac{3\sqrt{\chi}\omega_0^2}{2\omega_s^{1/2}\omega_a}, \quad (A6a)$$

$$K_{ssss} = \frac{7\chi\omega_0^2}{24\omega_s^2}, \quad K_{aaaa} = \frac{7\chi\omega_0^2}{24\omega_a^2}, \quad K_{ssaa} = \frac{7\chi\omega_0^2}{4\omega_s\omega_a}. \quad (A6b)$$

The coefficients relating normal coordinates to Cartesian coordinates are

$$\vec{t}_{Is} = \frac{1}{\sqrt{2m}} \hat{u}_I, \quad \vec{t}_{II s} = \frac{1}{\sqrt{2m}} \hat{u}_{II},$$

$$\vec{t}_{Ia} = \frac{1}{\sqrt{2m}} \hat{u}_I, \quad \vec{t}_{II a} = -\frac{1}{\sqrt{2m}} \hat{u}_{II},$$

where \mathbf{u}_I and \mathbf{u}_{II} are the unit vectors of bonds C_1H_I and $C_{II}H_{II}$, respectively.

We report here, for sake of completeness, the coefficients of the generating functions S_1 and S_2 :

$$S^{sss} = -(2/3)[K_{sss}/\omega_s \hbar^3],$$

$$S_{ss}^s = -[K_{sss}/\omega_s \hbar],$$

$$S^{saa} = -(2/\hbar^3)[K_{saa}/(4\omega_a^2 - \omega_s^2)](\omega_a^2/\omega_s),$$

$$S_{sa}^a = -(2/\hbar)[K_{saa}/(4\omega_a^2 - \omega_s^2)]\omega_a,$$

$$S_{aa}^s = -(1/\hbar)[K_{saa}/(4\omega_a^2 - \omega_s^2)](2\omega_a^2 - \omega_s^2)/\omega_s,$$

$$S_s^{sss} = -\frac{3}{16} \frac{2K_{ssss}\omega_s - 5K_{sss}^2}{\hbar^3 \omega_s^2},$$

$$S_a^{aaa} = -\frac{1}{16} \frac{6K_{aaaa}(\omega_s^3 - 4\omega_s\omega_a^2) + K_{saa}^2(8\omega_a^2 - 3\omega_s^2)}{\hbar^3(-4\omega_a^2 + \omega_s^2)\omega_a\omega_s},$$

$$S_{sss}^s = -\frac{1}{16} \frac{10K_{ssss}\omega_s - 9K_{sss}^2}{\hbar \omega_s^2},$$

$$S_{aaa}^a = -\frac{1}{16} \frac{10K_{aaaa}(\omega_s^3 - 4\omega_s\omega_a^2) + K_{saa}^2(8\omega_a^2 - 5\omega_s^2)}{\hbar(-4\omega_a^2 + \omega_s^2)\omega_a\omega_s},$$

$$S_s^{saa} = -\frac{1}{8} \frac{K_{ssaa}(\omega_s^4 - 4\omega_s^2\omega_a^2 - 8\omega_s\omega_a^3 + 2\omega_a\omega_s^3) + K_{saa}^2(8\omega_s\omega_a^2 + 2\omega_a\omega_s^2) + K_{saa}K_{sss}(10\omega_s\omega_a^2 - \omega_s^3 + 8\omega_a^3 - 2\omega_a\omega_s^2)}{(-4\omega_a^2 + \omega_s^2)(\omega_a + \omega_s)\hbar^3\omega_s^2},$$

$$S_{saa}^s = -\frac{1}{8} \frac{K_{ssaa}(3\omega_s^4 - 12\omega_s^2\omega_a^2 - 8\omega_s\omega_a^3 + 2\omega_a\omega_s^3) + K_{saa}^2 6\omega_a\omega_s^2 + K_{saa}K_{sss}(6\omega_s\omega_a^2 - 3\omega_s^3 + 8\omega_a^3 - 2\omega_a\omega_s^2)}{\hbar\omega_s^2(-4\omega_a^2 + \omega_s^2)(\omega_a + \omega_s)},$$

$$S_{ssa}^a = -\frac{1}{8}$$

$$\times \frac{K_{ssaa}(2\omega_s^4 - 8\omega_s^2\omega_a^2 - 12\omega_s\omega_a^3 + 3\omega_a\omega_s^3) + K_{saa}^2(6\omega_s\omega_a^2 + 4\omega_a\omega_s^2 - 4\omega_a^3) + K_{saa}K_{sss}(12\omega_s\omega_a^2 - 6\omega_s^3 + 10\omega_a^3 - 7\omega_a\omega_s^2)}{\hbar\omega_a\omega_s(-4\omega_a^2 + \omega_s^2)(\omega_a + \omega_s)},$$

$$S_a^{ssa} = -\frac{1}{8}$$

$$\times \frac{K_{ssaa}(2\omega_s^4 - 8\omega_s^2\omega_a^2 - 4\omega_s\omega_a^3 + \omega_a\omega_s^3) + K_{saa}^2(2\omega_s\omega_a^2 + 4\omega_a\omega_s^2 + 4\omega_a^3) + K_{saa}K_{sss}(12\omega_s\omega_a^2 - 6\omega_s^3 + 14\omega_a^3 - 5\omega_a\omega_s^2)}{(-4\omega_a^2 + \omega_s^2)(\omega_a + \omega_s)\hbar^3\omega_s^2}.$$

APPENDIX B: TRANSFORMED ELECTRIC DIPOLE MOMENT AND MAGNETIC DIPOLE MOMENT OPERATORS UP TO 2ND ORDER

We report here the terms in ε , ε^2 , and ε^3 of the transformed electric dipole moment and magnetic dipole moment operators [see Eqs. (11) and ff. and (16) and ff. in the text]:

$$\widehat{\vec{\mu}}_1^+ = \vec{\mu}_s q_s + \vec{\mu}_a q_a,$$

$$\widehat{\vec{\mu}}_2^+ = \frac{1}{2} \vec{\mu}_{ss} q_s^2 + \vec{\mu}_{sa} q_s q_a + \frac{1}{2} \vec{\mu}_{aa} q_a^2 + \vec{\mu}_s \hbar (S_{ss}^s q_s^2 + S_{aa}^s q_a^2 + S^{saa} p_a^2 + 3S^{sss} p_s^2) + \vec{\mu}_a \hbar (S_{sa}^a q_s q_a + 2S^{saa} p_s p_a),$$

$$\begin{aligned} \widehat{\vec{\mu}}_3^+ = & \vec{\mu}_{sa} \left(\hbar S_{aa}^s q_a^3 + \hbar S_{ss}^s q_s^2 q_a + \hbar S_{sa}^a q_s^2 q_a + 2\hbar S^{saa} \frac{1}{2} (q_s p_s + p_s q_s) p_a + 3\hbar S^{sss} p_s^2 q_a + \hbar S^{saa} \frac{1}{2} (q_a p_a^2 + p_a^2 q_a) \right) \\ & + \vec{\mu}_{aa} \left(2\hbar S^{saa} \frac{1}{2} (q_a p_a + p_a q_a) p_s + \hbar S_{sa}^a q_a^2 q_s \right) + \vec{\mu}_{ss} \left(\hbar S_{ss}^s q_s^3 + \hbar S_{aa}^s q_a^2 q_s + 3\hbar S^{sss} \frac{1}{2} (p_s^2 q_s + q_s p_s^2) + \hbar S^{saa} q_s p_a^2 \right) \\ & + \vec{\mu}_a \left(2\hbar S^{saa} \frac{1}{2} (q_s p_s + p_s q_s) p_a + \hbar S_{aa}^a q_a^3 + 3\hbar S_{aa}^{aaa} \frac{1}{2} (q_a p_a^2 + p_a^2 q_a) + \hbar S_{ssa}^a q_s^2 q_a + \hbar S_{sa}^{ssa} p_s^2 q_a + \frac{1}{2} \hbar^2 S_{aa}^s S_{sa}^a q_a^3 \right. \\ & + \frac{3}{2} \hbar^2 S^{sss} S_{sa}^a p_s^2 q_a - \frac{1}{2} \hbar^2 S_{sa}^a S^{saa} \frac{1}{2} (p_a^2 q_a + q_a p_a^2) + \frac{1}{2} \hbar^2 [(S_{sa}^a)^2 + S_{ss}^s S_{sa}^a] q_s^2 q_a - 2\hbar^2 S^{saa} S_{ss}^s \frac{1}{2} (q_s p_s + p_s q_s) p_a \\ & \left. - 2\hbar^2 S^{saa} S_{aa}^s p_s^2 q_a \right) + \vec{\mu}_s \left(\hbar S_{saa}^s q_a^2 q_s + 2\hbar S_{sa}^{saa} \frac{1}{2} (q_a p_a + p_a q_a) p_s + \hbar S_{sss}^s q_s^3 + \hbar^2 S_{sa}^a S_{aa}^s q_a^2 q_s + 3\hbar S_{ss}^{sss} \frac{1}{2} (q_s p_s^2 \right. \\ & + p_s^2 q_s) + \hbar^2 (S_{ss}^s)^2 q_s^3 + \hbar S_{sa}^{saa} p_a^2 q_s + \hbar^2 S_{aa}^s S_{ss}^s q_a^2 q_s - \hbar^2 S_{sa}^a S^{saa} p_a^2 q_s - 3\hbar^2 S^{sss} S_{sa}^a \frac{1}{2} (q_a p_a + p_a q_a) p_s \\ & \left. + \hbar^2 S^{saa} S_{ss}^s p_a^2 q_s - 3\hbar^2 S_{ss}^s S^{sss} \frac{1}{2} (p_s^2 q_s + q_s p_s^2) \right), \end{aligned}$$

$$\widehat{\vec{m}}_1^+ = \vec{\xi}_s p_s + \vec{\xi}_a p_a,$$

$$\begin{aligned} \widehat{\vec{m}}_2^+ = & \vec{\xi}_{ss} \frac{1}{2} (q_s p_s + p_s q_s) + \vec{\xi}_{aa} \frac{1}{2} (q_a p_a + p_a q_a) + \vec{\xi}_{sa} p_s q_a + \vec{\xi}_s p_a q_s + \vec{\xi}_s 2S_{ss}^s \hbar \left(2S_{ss}^s \frac{1}{2} (q_s p_s + p_s q_s) + S_{sa}^a \frac{1}{2} (q_a p_a + p_a q_a) \right) \\ & + \vec{\xi}_a \hbar (S_{sa}^a q_s p_a + 2S_{aa}^s q_a p_s), \end{aligned}$$

$$\begin{aligned} \widehat{\mathbf{m}}_3^+ = & \vec{\xi}_s \left(\hbar (\hbar S_{ss}^s S_{sa}^a - 2S_{ssa}^a) \frac{1}{2} (q_a p_a + p_a q_a) q_s - (S_s^{sss} + 3S_s^{sss} S_{ss}^s \hbar) \hbar p_s^3 + \hbar (\hbar S_{aa}^s S_{sa}^a - S_{saa}^s - S_{ss}^s S_{aa}^s \hbar) q_a^2 p_s \right. \\ & - \frac{3}{2} S_{sss}^s \hbar (q_s^2 p_s + p_s q_s^2) - [\hbar^2 (S_{ss}^s + S_{sa}^a) S_{saa}^s + S_s^{saa} \hbar] p_a^2 p_s + \hbar^2 (S_{ss}^s)^2 \frac{1}{2} (q_s^2 p_s + p_s q_s^2) \left. \right) + \vec{\xi}_a \left(\frac{1}{2} (\hbar^2 S_{sa}^a (S_{sa}^a - S_{ss}^s) \right. \\ & - 2S_{ssa}^s \hbar) q_s^2 p_a + \hbar (\hbar S_{ss}^s S_{aa}^s - S_{saa}^s) (q_s p_s + p_s q_s) q_a - \frac{1}{2} \hbar (4\hbar S_{ss}^s S_{aa}^s + 2S_{sa}^{saa} + 3S_s^{sss} S_{sa}^a \hbar) p_s^2 p_a + \frac{1}{2} \hbar \left(\frac{1}{2} S_{aa}^s S_{sa}^a \hbar \right. \\ & - 3S_{aaa}^a \left. \right) (q_a^2 p_a + p_a q_a^2) - \frac{1}{2} (2S_{aaa}^a + S_{ss}^s S_{sa}^a \hbar) \hbar p_a^3 \left. \right) + \vec{\xi}_s \left(\hbar (-2S_{ss}^s + S_{sa}^a) \frac{1}{2} (q_s p_s + p_s q_s) q_a + \hbar 2S_{ss}^s p_s^2 p_a \right. \\ & - \hbar S_{sa}^a \frac{1}{2} (q_a^2 p_a + p_a q_a^2) \left. \right) + \vec{\xi}_s \left((S_{ss}^s - S_{sa}^a) \hbar q_s^2 p_a - \hbar S_{aa}^s (q_s p_s + p_s q_s) q_a + S_{ss}^s \hbar p_a^3 + 3\hbar S_s^{sss} p_a p_s^2 + \frac{1}{2} \hbar S_{aa}^s (p_a q_a^2 \right. \\ & + q_a^2 p_a) + \vec{\xi}_{ss} \left(3S_s^{sss} \hbar p_s^3 + S_{ss}^s \hbar p_s p_a^2 - \frac{1}{2} S_{sa}^a \hbar q_s (q_a p_a + p_a q_a) + S_{aa}^s \hbar p_s q_a^2 - \frac{1}{2} S_{ss}^s \hbar (q_s^2 p_s + p_s q_s^2) \right) \\ & \left. + \xi_{aa} 2\hbar (S_{ss}^s p_s p_a^2 - S_{aa}^s p_s q_a^2) \right). \end{aligned}$$

APPENDIX C: ORIGIN INDEPENDENCE OF ROTATIONAL STRENGTHS FOR THE FIRST TWO OVERTONE TRANSITIONS

We have algebraically proved that rotational strengths are origin-independent for the transitions $0 \rightarrow 2$ and $0 \rightarrow 3$, under the assumption that $\vec{\mu}$ is a series expansion truncated to the second order, as in Eq. (11) in the text, and $\vec{\mathbf{m}}$, with respect to a generic origin point O , is given by Eq. (16) in the text, i.e.,

$$\vec{\mathbf{m}} = \frac{1}{2c} \sum_i (\vec{\mathbf{r}}_{Ai} \times \dot{\vec{\mu}}_i + \vec{\mu}_i \times \dot{\vec{\mathbf{r}}}_{Bi}), \quad i = \text{I, II}. \quad (\text{C1})$$

If the origin is shifted to another point O' , $\vec{\mathbf{m}}$ changes by the amount (in the case of two bonds, $i = \text{I, II}$):

$$\Delta \vec{\mathbf{m}} = \frac{1}{2c} (\vec{\mathbf{Y}} \times \dot{\vec{\mu}}_I + \vec{\mathbf{Y}} \times \dot{\vec{\mu}}_{II}), \quad (\text{C2})$$

where $\vec{\mathbf{Y}} = \vec{O'O}$. One has then to prove that the rotational strength arising out of this term is zero, i.e.,

$$\Delta \mathcal{R} = \text{Im}(\langle 0,0 | \vec{\mu}^+ | n_s, n_a \rangle \cdot \langle n_s, n_a | \Delta \vec{\mathbf{m}}^+ | 0,0 \rangle) = 0, \quad (\text{C3})$$

where $\Delta \vec{\mathbf{m}}^+$ is the transformed operator of Eq. (C2): we first have explicitly written an operator $\Delta \vec{\mathbf{m}}$ in Eq. (C2) in terms of bond parameters $\partial \vec{\mu}_i / \partial \ell_i|_0$ and $\partial^2 \vec{\mu}_i / \partial \ell_i^2|_0$ [see Eqs. (16) and (17) and ff. in the text]. Then we have derived $\vec{\mu}^+$ and $\Delta \vec{\mathbf{m}}^+$ according to Eq. (21) in the text considering terms up to $\vec{\mu}_3^+$ and $\Delta \vec{\mathbf{m}}_3^+$.

The proof was carried out with the algebraic manipulator MAPLE for the two manifolds $n_s + n_a = 2$ and $n_s + n_a = 3$. It turns out that every couple of values for n_s, n_a within the second and third manifold yields $\Delta \mathcal{R} = 0$ identically. We may remark that the U matrix need not be applied, since it does not affect the result, being a linear operator.

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