

Calculated Absorption and Vibrational Circular Dichroism Spectra of Fundamental and Overtone Transitions for a Chiral HCCH Molecular Fragment in the Hypothesis of Coupled Dipoles

ROBERTO GANGEMI, GIOVANNA LONGHI, AND SERGIO ABBATE*

Dipartimento di Scienze Biomediche e Biotecnologie, Università di Brescia, Brescia, Italy

Dedicated to Prof. Piero Salvadori, Pisa, on the occasion of his 70th birthday.

ABSTRACT We establish the general behavior of absorption and vibrational circular dichroism spectra (VCD) of a chiral HCCH fragment lacking all symmetry elements; the study is limited to CH-stretching modes, and the Hamiltonian employed is written in terms of normal-mode coordinates and momenta and approximates two different Morse oscillators interacting through a harmonic coupling term; rotational strengths are evaluated within a hypothesis of coupled electric dipoles. Van Vleck contact transformations written in terms of raising and lowering operators are used to calculate spectra up to the manifold $\Delta v = 4$. Three transformations are necessary to obtain fourth-order terms in the relevant operators, namely, the electric and magnetic dipole moments. The dynamics of the system exhibits 1:1 resonance terms in addition to the Darling–Dennison coupling term. We discuss the importance of coupling between CH stretches with respect to differences in their local mechanical characteristics in determining the aspect of the absorption and VCD fundamental and overtone spectra of increasing quantum number. © 2005 Wiley-Liss, Inc. *Chirality* 17:530–539, 2005.

KEY WORDS: vibrational circular dichroism (VCD); CH stretching; overtones; near infrared (NIR); local modes; normal modes; Van Vleck perturbation theory

STATEMENT OF THE PROBLEM AND METHOD

In collaboration with Professor Salvadori's group, some years ago we measured the vibrational circular dichroism (VCD) spectra in the near-infrared (NIR) range of some limonene-like compounds¹ ($\Delta v = 3, 4$) and of cyclic ketones² ($\Delta v = 2, 3, 4$). Establishing whether any behavior was common to the various overtone orders and what kinds of relations exist in the fundamental CH-stretching region were important theoretical goals.

In a previous paper,³ we tackled this theoretical goal by applying the Van Vleck perturbative method⁴ to the study of the CH-stretching vibrational dynamics of the molecular fragment HCCH with C_2 symmetry; specifically, we modeled the fragment as two coupled anharmonic oscillators with the same mechanical frequencies, the same anharmonicities, etc. A wholly algebraic treatment of the problem was made possible by the computer-based algebraic manipulator Maple.⁵ In this way, we could obtain analytical expressions for frequencies (ω), dipole strengths (D), and rotational strengths (R) for CH-stretching transitions with $\Delta v = 1, 2, 3$. Actually, experimentalists can measure rotational strengths for overtone spectra at least up to $\Delta v = 4$ ^{1,2,6–8} and dipole strengths much further;^{9,10} besides, most experimental data involve a variety of molecular fragments that not only

are dyssymmetric but are quite asymmetric and possess many degrees of freedom. In the present paper, our purpose is to extend our study to the third overtone, $\Delta v = 4$, on one hand and, on the other hand, to a fragment that still possesses two degrees of freedom but which is made up of CH oscillators that have two different mechanical frequencies and/or two different anharmonicities. The motivation of the latter generalization is that we wish to compare with NIR-VCD data of ring molecules, for which it is known that mechanical frequencies, anharmonicity constants, and bond lengths are different for axial and equatorial CH bonds.^{10–12} Thus, the HCCH fragment discussed herein might be found in 6- or 5-membered ring molecules, like (3*R*)-(+)-methylcyclohexanone and (3*R*)-(+)-methylcyclopentanone, with an axial CH at one end and an equatorial CH at the other end.

In Professor Salvadori's laboratory in 1985, two of us (S.A. and G.L.) made the first VCD measurements in the range 1300–800 nm.

*Correspondence to: Sergio Abbate, Dipartimento di Scienze Biomediche e Biotecnologie, Università di Brescia, Viale Europa 11, 25123 Brescia, Italy. E-mail: abbate@med.unibs.it

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These generalizations require that few more terms be formally included in the Hamiltonian of Ref. 3, which is written as a fourth-order Taylor expansion in normal coordinates q_+ , q_- (vide infra):

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

The different oscillators C_1H_1 and C_2H_2 , are modeled as Morse oscillators in local coordinates l_1 and l_2 ,¹³ with distinct mechanical frequencies ω_{01} and ω_{02} and/or distinct anharmonicity constants χ_1 and χ_2 . The two local Morse oscillators are supposed to be linearly coupled via a harmonic interaction force constant, K_{12} .^{3,10,14,15} We can then write the terms of Eq. (1) as follows:

$$H_0 = \frac{hc}{2} \left[\omega_+ \left(\frac{p_+^2}{\hbar^2} + q_+^2 \right) + \omega_- \left(\frac{p_-^2}{\hbar^2} + q_-^2 \right) \right], \quad (2')$$

$$\varepsilon H_1 = hc [K_{+++} q_+^3 + K_{---} q_-^3 + K_{+-} q_+^2 q_- + K_{-+} q_-^2 q_+], \quad (2'')$$

$$\varepsilon^2 H_2 = hc [K_{++++} q_+^4 + K_{----} q_-^4 + K_{+--+} q_+^2 q_-^2 + K_{-++-} q_-^2 q_+^2], \quad (2''')$$

where q_+ , p_+ , q_- , and p_- are the dimensionless coordinate and conjugated momentum operators associated with the higher- and lower-frequency normal modes; they reduce respectively to symmetric and antisymmetric combinations of bond-stretching coordinates (or momenta) in the case of identical oscillators and for $K_{12} > 0$. The normal-mode frequencies are

$$\omega_+^2 = \frac{\omega_{01}^2 + \omega_{02}^2}{2} + \frac{1}{2} \sqrt{(\omega_{01}^2 - \omega_{02}^2)^2 + \frac{K_{12}^2}{4\pi^4 c^4 m^2}}$$

and

$$\omega_-^2 = \frac{\omega_{01}^2 + \omega_{02}^2}{2} - \frac{1}{2} \sqrt{(\omega_{01}^2 - \omega_{02}^2)^2 + \frac{K_{12}^2}{4\pi^4 c^4 m^2}}$$

In these equations, $m = (12/13)$ amu is the reduced mass of each CH bond, and c is the speed of light. The constants K_{+++} through K_{-+-} in Eqs. (2'') and (2''') can be written in terms of ω_{01} , ω_{02} , χ_1 , and χ_2 and K_{12} , analogously to that done, e.g., in Ref. 3 (see Appendix I). The terms with an odd number of “-” are 0 in the case of identical oscillators and $K_{12} > 0$.

The use of Morse oscillators to model local anharmonic oscillators, while not strictly necessary, allows easy definition of the parameters ω_{0i} and χ_i .¹³ Indeed, the expansion in Eq. (1) is stopped at fourth order and the use of coupled fourth-order generic anharmonic oscillators in principle would be satisfactory as long as the third-order term in the potential were opposite the second- and fourth-order terms, with relations between expansion coefficients as required by the Morse potential.¹³⁻¹⁶

The Van Vleck method consists of transforming the Hamiltonian to a new representation in which only degenerate (or nearly degenerate) states are coupled. The effective Hamiltonian, $H^{(n)}$, obtained after n Van Vleck transformations, as well as the effective operators $\mu^{(n)}$ and $m^{(n)}$ needed for calculating dipole and rotational strengths, can be obtained^{3,4} by

$$H^{(n)} = T_n \dots T_1 H T_1^{-1} \dots T_n^{-1}, \quad \text{with } T_n = e^{ie^n S_n}. \quad (3)$$

As pointed out in Ref. 3, fourth-order expansion of the electric and magnetic dipole moments is required to obtain non-zero intensity at $\Delta v = 4$, which makes it necessary to perform at least three contact transformations: T_1 , T_2 , and T_3 . The generating function S_1 and likewise S_2 was determined for the simple Hamiltonian of Ref. 3 by requiring the off-diagonal terms of the matrix elements generated by the once (and then twice)-transformed Hamiltonian to be zero. In order to determine the generating function coefficients³ by this method, an equal number of independent conditions in the matrix elements must be found. Because finding an entire set of independent equations proves to be pretty difficult, even more so as the order of S increases, we came to consider the approach expounded upon here in and used in a number of instances described by Sibert (see e.g. Ref. 17), in which the raising and lowering operators a^\dagger and a are employed instead of p and q . The relations for raising and lowering operators a_+^\dagger , a_-^\dagger and a_+ , a_- to q_+ , p_+ , and q_- , p_- are as follows:

$$q_+ = \frac{1}{\sqrt{2}} (a_+ + a_+^\dagger), \quad \frac{p_+}{\hbar} = \frac{i}{\sqrt{2}} (a_+ - a_+^\dagger), \quad (4)$$

$$q_- = \frac{1}{\sqrt{2}} (a_- + a_-^\dagger), \quad \frac{p_-}{\hbar} = \frac{i}{\sqrt{2}} (a_- - a_-^\dagger). \quad (4')$$

Basically, the advantage of this approach lies in the fact that determination of the S functions is made much easier: the conditions can be imposed directly on operators instead of on matrix elements; the expressions for the perturbative terms as well as for the S function are more compact; and, most importantly, they are formally the same for each successive transformation (vide infra). The convention adopted in order to have a univocal form for the transformed operators is that all a^\dagger operators precede the a operators in the single terms of the summation, i.e., the normal form, as defined in Ref. 17, is to be used. This can always be done by exploiting the commutation rule, $[a, a^\dagger] = 1$. So, by way of example, one obtains for H_1 :

$$\varepsilon H_1 = \sum_{\substack{\mathbf{m}, \mathbf{n} \\ |\mathbf{m}| + |\mathbf{n}| \leq 3}} c_{\mathbf{m}, \mathbf{n}} a^{\dagger \mathbf{m}} a^{\mathbf{n}}, \quad (5)$$

having introduced the arrays of integers $\mathbf{m} = \{m_+, m_-\}$, $\mathbf{n} = \{n_+, n_-\}$, with $|\mathbf{m}| + |\mathbf{n}| = m_+ + m_- + n_+ + n_-$, where when we write $a^{\dagger \mathbf{m}} a^{\mathbf{n}}$ we mean $a_+^{\dagger m_+} a_+^{\dagger m_-} a_+^{n_+} a_+^{n_-}$. Coefficients $c_{\mathbf{m}, \mathbf{n}}$ are functions of K_{+++} , K_{+-} , etc., and are obtained from Eqs. (2''), (4), and (4') and by reordering the operators. Out of this expression, S_1 can be easily deduced by a

choice of all of those addenda, whose denominators are non-zero, through the following equation¹⁷:

$$S_1 = \sum_{\substack{\mathbf{m}, \mathbf{n} \\ |\mathbf{m}| + |\mathbf{n}| \leq 3}}'' \frac{c_{\mathbf{m}, \mathbf{n}} a^{i\mathbf{m}} a^{\mathbf{n}}}{i\hbar(\mathbf{m} - \mathbf{n}) \cdot \omega}, \quad (6)$$

where we have introduced $\omega = \{\omega_{01}, \omega_{02}\}$. The symbol Σ'' means that the sum is over the subset of all terms belonging to H_1 with \mathbf{m}, \mathbf{n} such that $(\mathbf{m} - \mathbf{n}) \cdot \omega \neq 0$; Σ' is employed, instead of denoting a sum that is extended over the remaining terms of H_1 , namely, the ones forming the transformed Hamiltonian, $H_1^{(1)}$:

$$H_1^{(1)} = \sum_{\substack{\mathbf{m}, \mathbf{n} \\ |\mathbf{m}| + |\mathbf{n}| \leq 3}}' c_{\mathbf{m}, \mathbf{n}} a^{i\mathbf{m}} a^{\mathbf{n}}. \quad (7)$$

The transformed Hamiltonian $H^{(1)} = H_0 + \varepsilon H_1^{(1)} + \varepsilon^2 H_2^{(1)}$ is obtained through the use of Eq. (3). In our case, $H_1^{(1)} = 0$. The procedure is iterated for $H_2^{(1)}$, reduced to "normal form" as in Eq. (5), to build S_2 and $H_2^{(2)}$, which will be given by equations that are formally identical to Eqs. (6) and (7), respectively.

We then generated the final expression for the transformed Hamiltonian $H^{(3)}$, and for S_3 in a and a^\dagger up to third order:

$$H^{(3)} = H_0 + \varepsilon H_1^{(3)} + \varepsilon^2 H_2^{(3)} + \varepsilon^3 H_3^{(3)}$$

Complete expressions for $H_n^{(2)}$ and $H_n^{(3)}$ are too long to report here. In Appendix II, we compare the simple and physically meaningful $H_0 + H_2^{(2)}$ with what has already been reported in the literature¹⁸ by variational methods. In fact, $H_0 + H_2^{(2)}$ is the usual second-order Hamiltonian in terms of a and a^\dagger and is the Darling–Dennison Hamiltonian in the case of identical oscillators. We also point out that, with the two oscillators being different, the terms $q_+ q_-^3$ and $q_-^3 q_+$ of Eq. (2'') generate a new 1:1 resonance for $\omega_+ \approx \omega_-$ besides the Darling–Dennison 2:2 resonance due to $q_+^2 q_-^2$. This resonance had already been shown by Lehmann¹⁹ in studying HCN and DCN and is also important in determining the absorption spectra of molecules with similar but not identical oscillators; Lehmann himself advised that this resonance in the presence of inequivalent CH-bond stretches be taken into account. An interesting case of this, for example, is that of n -paraffins that contain CH_2 s with slightly different CH bonds due to missing overall σ symmetry generated by conformational disorder,²⁰ as is the case of cyclic molecules described above.^{10–12}

RESULTS AND DISCUSSION

Because this work is concerned with the intensity and rotational strength calculations of overtones, we need apply every contact transformation defined by Eq. (3) to the electric and magnetic dipole moments $\boldsymbol{\mu}$ and \mathbf{m} , which are usually described in terms of q and p operators. For this reason we have written S_1 , S_2 , and S_3 in terms of q and p ; numerical substitutions of all parameters was needed due to the size of the algebraic expression of S_3 coeffi-

cients. To calculate dipole and rotational strengths, we must first prescribe the functional dependence of electric and magnetic moment operators on coordinates and momenta. A general Taylor expansion of $\boldsymbol{\mu}$ and \mathbf{m} in q_\pm and p_\pm can be used in principle. However, in order to explicitly define the expansion coefficients and to build corresponding spectra, we have chosen here a bond approximation model for $\boldsymbol{\mu}$ and \mathbf{m} (i.e., we represent molecular dipoles as sums of bond dipoles); further, we have assumed the coupled dipole model for rotational strengths.^{3,21} We are well aware of the limitations of this model and quite recently, we examined examples wherein the bond approximation for the rotational strengths of overtones proves to be inadequate²²; however, the simplicity of this model permits us to use a low number of parameters: these are the first and second derivatives of the CH-bond electric dipole moment with respect to the bond-stretching coordinates and they may be evaluated experimentally from overtone intensities.^{12,14–16} In the present case, we use an extension of the coupled-dipoles model presented in Ref. 21, allowing for electrical anharmonicity. The actual values of bond-moment parameters are taken from Ref. 12. Values of the geometric parameters for the HCCH fragment are reported in the footnote of Table 1 and are the same as in Ref. 3; for dynamic parameters, see below. Transition moments of the transformed operators have to be evaluated with the eigenstates of the transformed Hamiltonian, $H^{(3)}$. Because the matrix associated with $H^{(3)}$ is not diagonal due to 1:1 and 2:2 resonances, one proceeds to calculate the eigenvalues (energy levels) and eigenvectors (vibrational modes) on which transition moments have to be evaluated.

As expected from what happens for isolated Morse oscillators,¹³ the values of energies for levels through $\Delta v = 4$ are not modified by third-order terms in ε .¹⁰ Regarding dipole and rotational strengths, for $\Delta v = 1$ and $\Delta v = 3$ they are not affected by the fourth-order terms in ε ; on the contrary, at $\Delta v = 2$ and $\Delta v = 4$, there are corrections in the ε^4 terms due to the introduction of S_3 . This can be appreciated by comparing column A of Table 1 relative to the case of identical oscillators with the results of Table IV in Ref. 3. Because we want to illustrate the behavior of the dipole and rotational strengths upon increasing the difference between the oscillators' intrinsic parameters, we report in Table 1 (columns B and E) the output of four parameters' sets for very closely chosen values for local frequencies ω_{01} and ω_{02} around 3000 cm^{-1} , anharmonicities χ_1 and χ_2 around 60 cm^{-1} and two values for the interaction force constant K_{12} ($+0.065$ and $+0.26 \text{ mdyne/\AA}$). The first value for K_{12} has been chosen to ensure a separation of 40 cm^{-1} between the fundamental frequencies in the case $\omega_{01} = \omega_{02} = 3000 \text{ cm}^{-1}$; we observe that the chosen value for K_{12} is not unreasonable as it compares well with experimental values for direct couplings between CH stretches in n -paraffins, as reported in Refs. 23 and 24; the second value instead has been chosen to be four times the first one, in order to compensate for the observed loss of intensity in rotational strengths. The chosen values for ω_{01} , ω_{02} , χ_1 , χ_2 should also be compared with the values obtained, e.g., for axial and equatorial CH of cyclohexane

TABLE 1. Calculated frequencies ω (cm^{-1}), dipole strengths (D) ($\text{esu}^2 \text{cm}^2$), and rotational strengths (R) ($\text{esu}^2 \text{cm}^2$) for several values of mechanical frequencies and anharmonicities in a system of two coupled oscillators*

| A | | | B | | | C | | | D | | | E | | |
|--|-----------------|------------------|--|-----------------|------------------|--|-----------------|------------------|---|-----------------|------------------|---|-----------------|------------------|
| $\omega_{01} = 3000, \omega_{02} = 3000, \chi_1 = \chi_2 = 60,$ $K_{12} = 0.065 \text{ mdyne}/\text{\AA}$ | | | $\omega_{01} = 2995, \omega_{02} = 3005, \chi_1 = \chi_2 = 60,$ $K_{12} = 0.065 \text{ mdyne}/\text{\AA}$ | | | $\omega_{01} = \omega_{02} = 3000, \chi_1 = \chi_2 = 65,$ $K_{12} = 0.065 \text{ mdyne}/\text{\AA}$ | | | $\omega_{01} = 2995, \omega_{02} = 3005, \chi_1 = \chi_2 = 60,$ $K_{12} = 0.26 \text{ mdyne}/\text{\AA}$ | | | $\omega_{01} = \omega_{02} = 3000, \chi_1 = 55, \chi_2 = 65,$ $K_{12} = 0.26 \text{ mdyne}/\text{\AA}$ | | |
| ω | D | R | ω | D | R | ω | D | R | ω | D | R | ω | D | R |
| 2861 | 0.23E-38 | -0.19E-42 | 2861 | 0.24E-38 | -0.18E-42 | 2859 | 0.25E-38 | -0.17E-42 | 2804 | 0.24E-38 | -0.19E-42 | 2803 | 0.24E-38 | -0.19E-42 |
| 2902 | 0.46E-38 | 0.19E-42 | 2903 | 0.46E-38 | 0.18E-42 | 2904 | 0.45E-38 | 0.17E-42 | 2966 | 0.45E-38 | 0.19E-42 | 2967 | 0.45E-38 | 0.19E-42 |
| 5631 | 0.23E-40 | 0.18E-44 | 5626 | 0.21E-40 | 0.90E-45 | 5608 | 0.17E-40 | 0.29E-45 | 5540 | 0.15E-40 | 0.11E-44 | 5535 | 0.14E-40 | 0.10E-44 |
| 5643 | 0.13E-40 | -0.20E-44 | 5648 | 0.15E-40 | -0.11E-44 | 5666 | 0.18E-40 | -0.53E-45 | 5649 | 0.13E-40 | -0.21E-44 | 5653 | 0.14E-40 | -0.20E-44 |
| 5779 | 0.24E-41 | 0.19E-45 | 5779 | 0.24E-41 | 0.19E-45 | 5780 | 0.27E-41 | 0.20E-45 | 5895 | 0.91E-41 | 0.75E-45 | 5896 | 0.94E-41 | 0.74E-45 |
| 8279 | 0.16E-41 | -0.41E-45 | 8265 | 0.24E-41 | -0.20E-46 | 8220 | 0.25E-41 | -0.47E-47 | 8192 | 0.14E-41 | -0.28E-45 | 8163 | 0.19E-41 | -0.13E-45 |
| 8280 | 0.33E-41 | 0.41E-45 | 8294 | 0.25E-41 | 0.22E-46 | 8339 | 0.24E-41 | 0.78E-47 | 8251 | 0.30E-41 | 0.36E-45 | 8277 | 0.24E-41 | 0.21E-45 |
| 8497 | 0.37E-43 | -0.95E-47 | 8496 | 0.37E-43 | -0.95E-47 | 8492 | 0.37E-43 | -0.97E-47 | 8497 | 0.44E-42 | -0.11E-45 | 8497 | 0.47E-42 | -0.11E-45 |
| 8578 | 0.42E-43 | 0.54E-47 | 8579 | 0.42E-43 | 0.54E-47 | 8583 | 0.49E-43 | 0.49E-47 | 8772 | 0.20E-42 | 0.27E-46 | 8774 | 0.21E-42 | 0.27E-46 |
| 10801 | 0.31E-42 | 0.51E-46 | 10782 | 0.23E-42 | 0.71E-49 | 10702 | 0.26E-42 | -0.29E-49 | 10726 | 0.24E-42 | 0.18E-46 | 10652 | 0.25E-42 | 0.26E-47 |
| 10802 | 0.15E-42 | -0.52E-46 | 10821 | 0.23E-42 | -0.18E-48 | 10901 | 0.20E-42 | -0.87E-49 | 10766 | 0.18E-42 | -0.22E-46 | 10836 | 0.16E-42 | -0.78E-47 |
| 11149 | 0.26E-44 | 0.44E-48 | 11146 | 0.24E-44 | 0.39E-48 | 11116 | 0.19E-44 | 0.18E-48 | 11058 | 0.44E-43 | 0.75E-47 | 11052 | 0.46E-43 | 0.80E-47 |
| 11181 | 0.13E-44 | -0.45E-48 | 11184 | 0.14E-44 | -0.39E-48 | 11211 | 0.19E-44 | -0.17E-48 | 11278 | 0.11E-43 | -0.37E-47 | 11284 | 0.12E-43 | -0.36E-47 |
| 11335 | 0.27E-45 | -0.47E-49 | 11335 | 0.27E-45 | 0.47E-49 | 11338 | 0.37E-45 | 0.49E-49 | 11601 | 0.32E-44 | 0.56E-48 | 11604 | 0.34E-44 | 0.56E-48 |

*In all cases, the oscillators have the same first and second derivatives of the electric dipole moment with respect to the bond length ($\partial\mu/\partial l = -0.143e, \partial^2\mu/\partial l^2 = -0.485e/\text{\AA}$). The two valence angles of the HCC fragment are 109.47° ; the dihedral angle is $\varphi = 60^\circ$. The C-C bond length is 1.54 \AA . In case A, the differences in frequencies with Ref. 3 are less than 1 per 1000, due to different definitions of interaction force constants. Values of D and R coincide with the values in Ref. 3 = at $\Delta v = 1$ and 3 and are modified by the introduction of terms generated by S_3 at $\Delta v = 2$ or 4 (see text).

by NIR–local-mode spectroscopy; indeed in Ref. 10: $\omega_{01} = 3004 \text{ cm}^{-1}$, $\omega_{02} = 3037 \text{ cm}^{-1}$, $\chi_1 = 63.1 \text{ cm}^{-1}$, $\chi_2 = 62.1 \text{ cm}^{-1}$. One may notice that, on increasing the difference between the mechanical frequencies of the CH bonds (ω_0) (column B) and between their anharmonicities (χ) (column C), the calculated rotational strengths tend to be 1 order of magnitude below those of column A, from the second overtone and upward, signaling that the oscillators can be thought of as uncoupled. If the mechanical frequencies ω or the anharmonicity constants χ are too close (column A), then the two lowest-lying features in overtone manifolds, although they exhibit rotational strengths of the correct order of magnitude,¹ are unobservable, since the two bands of opposite sign tend to cancel out, having almost the same frequencies. In a coupled-oscillator model, to ensure observability of a high overtone VCD for molecules containing an HCCH fragment, the mechanical characteristics of CH bonds should be sufficiently similar to favor interaction but not too much, in order to avoid degeneracy. Alternatively, if we increase the coupling constant K_{12} (and leave all other parameters unaltered), the rotational strengths rise again (see columns D and E). Incidentally we notice that, assuming the same value for $\chi_1 - \chi_2$ and for $\omega_{01} - \omega_{02}$, one obtains a greater effect at higher overtone order in the first case, because the effect of anharmonicity goes

with the square of vibrational quantum number v , while the effect of mechanical frequency is linear in v .

The main issues of the present study in relation to the overtone VCD spectra are as follows: (a) Is it possible to associate observed VCD spectra with normal mode states at high overtones ($\Delta v > 2$), and what do the predicted spectra look like? (b) What is the relation between the VCD spectra of a manifold at a given Δv with the one at $(\Delta v + 1)$? For this purpose, it is worthwhile to consider Figure 1, where we report the graphical representation of the results for absorption and VCD spectra corresponding to columns C (top of the Figure) and E (bottom) of Table 1; therein we have prescribed a Lorentzian bandshape to each predicted transition, following the indications of Ref. 25. One may appreciate from the second line of the figure that VCD spectra corresponding to case C of Table 1 for two coupled oscillators are practically unobservable beyond $\Delta v = 2$; indeed, at $\Delta v = 3$ and 4, the order of magnitude of predicted VCD features is too little to make the calculated features observable. This is ultimately due to the small value of K_{12} causing too little coupling between oscillators. With the assumption of coupled-dipole mechanism in generating rotational strengths, the conditions to expect observability of VCD are a greater value for the interaction force constant in addition to a sufficient difference in the

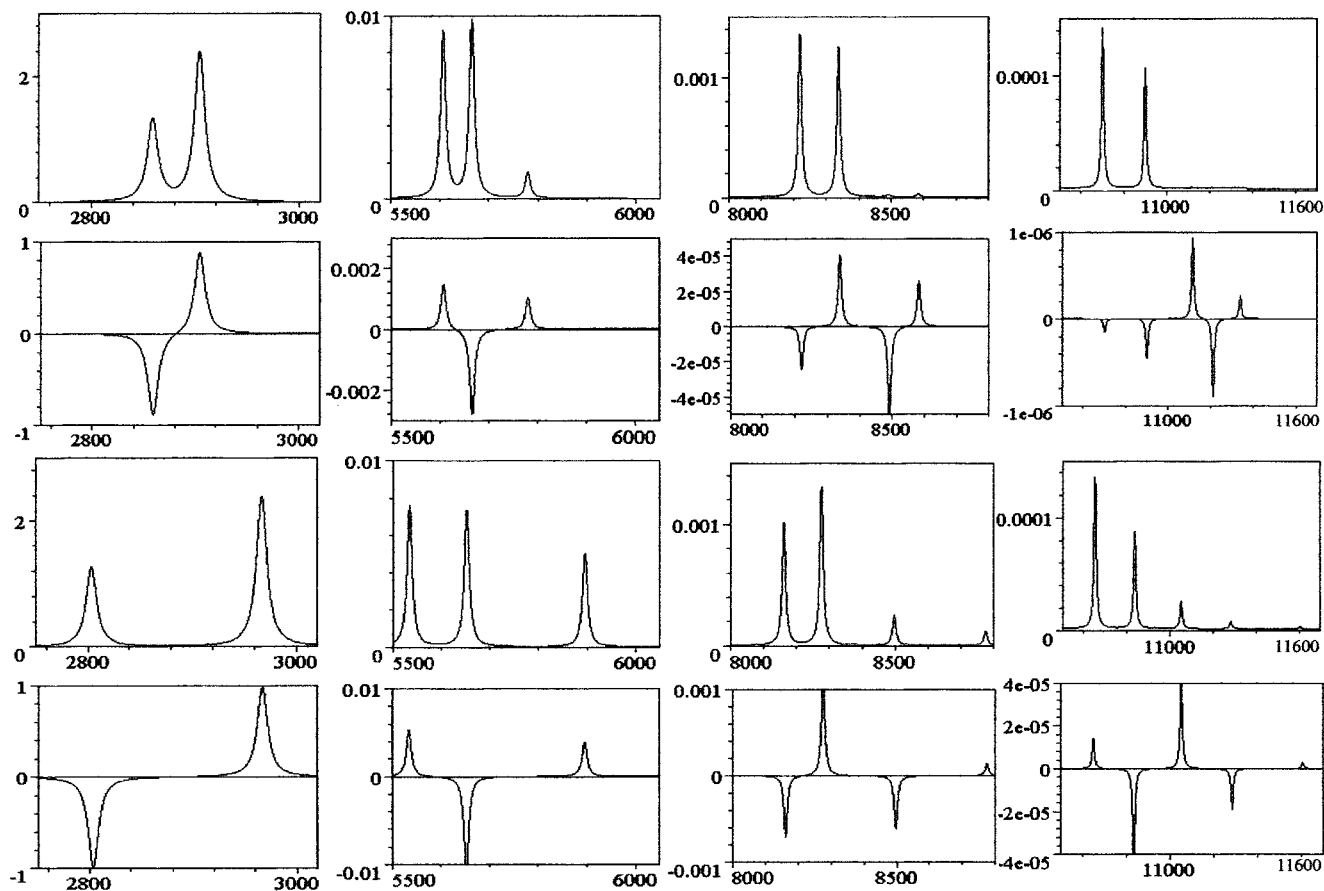


Fig. 1. Calculated absorptions and VCD spectra for the set C (first pair of rows) and set E (second pair) of Table 1 with $K_{12} > 0$. Abscissae are in wavenumber units; band areas are the calculated dipole strengths given in units of $10^{-40} (\text{esu cm})^2$, and the calculated rotational strengths in units of $10^{-44} (\text{esu cm})^2$. The bandshape is Lorentzian with a constant half-width at half-height of 6 cm^{-1} for all overtone orders.

mechanical frequencies and/or anharmonicities of the two bonds. In comparing the results for cases C and E of Table 1 and Figure 1, one sees that the absorption features—in both cases—and the VCD features (just in case E) decrease by 2 orders of magnitude in going from the fundamental ($\Delta v = 1$) to the first overtone region ($\Delta v = 2$) and by 1 order of magnitude for each successive overtone region. This corresponds to experiment.^{1,2,6-8} Besides, the separation of calculated VCD features at $\Delta v = 3$ (ca. 100 cm^{-1}) is in line with current experimental resolution^{7,8,22}: in the case of camphor we observed bands separated ca. 100 cm^{-1} , in the case of α -pinene ca. 60 cm^{-1} . Examination of Figure 1 allows one to appreciate further characteristics of the spectroscopic behavior of chirally disposed coupled oscillators at the fundamental and overtone orders. The following observations can be made on these numerical examples: (i) at $\Delta v = 2$ and in many cases for $\Delta v = 3$, the two largest VCD features are associated with the two lowest-frequency features, that are usually described as due to the two local modes of the two CH bonds; these bands have some VCD, inasmuch as they preserve some dynamical coupling (cf. Ref. 3); (ii) from $\Delta v = 4$, this is no longer true, even though the main absorption features are still those for the overtone “local” modes; (iii) the VCD doublet associated with the two lowest-frequency features alternates in sign going from manifold v to manifold $v + 1$; this is due to the positive sign of K_{12} . We report in Figure 2

the cases with the same parameters as for cases C and E of Figure 1, except that the K_{12} parameter is negative. One may notice that for negative K_{12} the lowest-frequency doublet preserves the sign with increasing v . This fact had been already pointed out on a semiclassical basis²⁶; (iv) at $\Delta v = 2$ the feature at highest frequency, which is generally thought of as the (1,1) combination band in the local-mode quantum numbers, is predicted to be quite strong also in absorption when $K_{12} = 0.26 \text{ mdyne/\AA}$, and this may have something to do with the puzzlingly intense (1,1) combination bands observed in polyethylene and in *n*-paraffins.²⁰

To explain sign alternation between successive manifolds in the case of positive K_{12} (point iii above), one may notice that the character of the mode associated with the lowest-frequency feature alternates, i.e., at $\Delta v = 1$ it is mainly (in terms of local mode quantum numbers) $|1,0_{>1}-0,1_{>1}$, at $\Delta v = 2$ it is mainly $|2,0_{>1}+0,2_{>1}$, at $\Delta v = 3$ it is mainly $|3,0_{>1}-0,3_{>1}$, and so forth; for the second-lowest-frequency feature, at $\Delta v=1$ we checked that it is mainly $|1,0_{>1}+0,1_{>1}$, at $\Delta v = 2$ it is mainly $|2,0_{>1}-0,2_{>1}$, at $\Delta v = 3$ it is mainly $|3,0_{>1}+0,3_{>1}$, and so on. The transformation from normal mode basis to local mode basis can be achieved following the procedure illustrated at the end of Section II of Ref. 3. The fact that the mostly antisymmetric mode has the lowest frequency at $\Delta v = 1$ for $K_{12} > 0$ and the mostly symmetric one has the lowest frequency at $\Delta v = 1$ for $K_{12} < 0$ is established by the equation preceding Eq. (3) in the

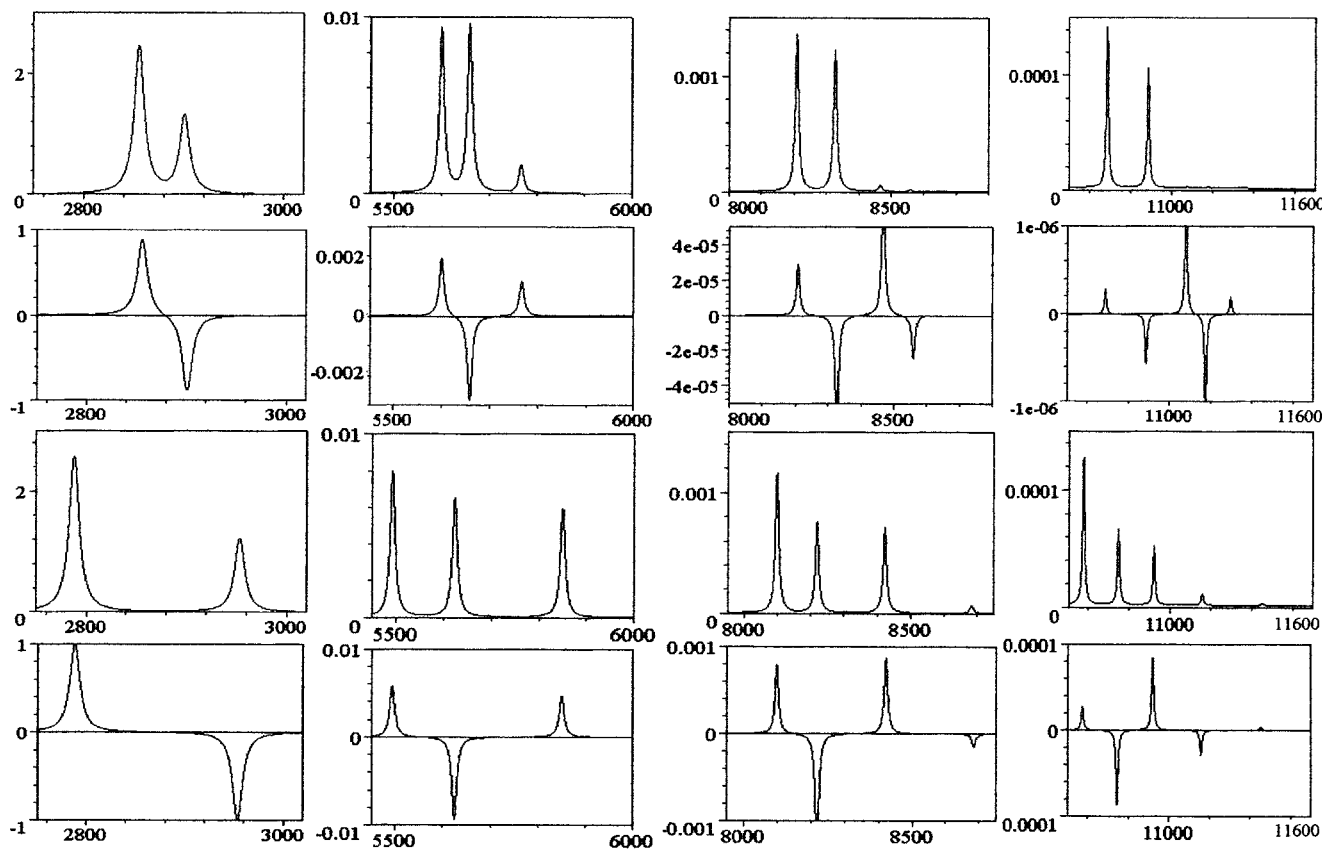


Fig. 2. Calculated absorptions and VCD spectra for set C (first pair of rows) and set E (second pair) of Table 1 with $K_{12} < 0$. Abscissae are in wavenumber units; band areas are the calculated dipole strengths given in units of $10^{-40} (\text{esu cm})^2$, and the calculated rotational strengths in units of $10^{-44} (\text{esu cm})^2$. The bandshape is Lorentzian with a constant half-width at half-height of 6 cm^{-1} for all overtone orders.

text and by the results of Appendix I. Indeed, before the Darling–Dennison resonance takes place, the frequency order of $|0, v_{>1} \pm |v, 0_{>1}$ at each manifold v is the same as $|0, 1_{>1} \pm |1, 0_{>1}$, but that resonance, taking place for submanifolds of separate symmetries, reorders the states; this is true for positive K_{12} values typical of CH-stretching oscillators. The reordering is such that at even values of v the symmetric combination $|0, v_{>1} + |v, 0_{>1}$ is at the lowest frequency, at odd values of v the lowest-frequency feature is the antisymmetric one $|0, v_{>1} - |v, 0_{>1}$. This is due to the fact that at even orders the symmetric block of the manifold contains one more state than the antisymmetric one, namely the $|v/2, v/2_{>1}$ state. This state “pushes” the symmetric local mode combination to low frequencies. This rule ceases to be obeyed at higher overtones due to higher congestion of interacting states.³ As noticed above, the sign alternation is not present with $K_{12} < 0$ since the lowest-lying feature is the symmetric combination before and after Darling–Dennison resonance: indeed we verified that for all manifolds the lowest-frequency feature is the symmetric one, as is expected, and its VCD is always positive with the present geometry.

The eigenvectors written in terms of local mode coordinates allow one also to appreciate why major absorption features and major VCD features do not necessarily coincide (observation ii above). In the case of different oscillators we have verified that within each manifold the two lowest-frequency features have local mode character, that is to say the contribution in local mode eigenvectors is either from local mode $|v, 0_{>1}$ or from

$|0, v_{>1}$, while at higher frequencies the contribution of $|v, 0_{>1}$ or $|0, v_{>1}$ (these are the modes bringing in intensity in the present bond approximation) is more evenly distributed, even if it is low. This is the reason why in each overtone region not necessarily observed VCD bands correspond to the most intense absorption bands. To be more specific, let us denote by c_{1v} and c_{2v} the coefficients multiplying $|v, 0_{>1}$ and $|0, v_{>1}$ respectively, for a given wavefunction ψ at a given overtone order v . Within the bond dipole moment hypothesis, one may show that the dipole strength D_ψ , the rotational strength R_ψ , and the g factor for the transition from the ground state to ψ are:

$$D_\psi = \mu_v^2 [c_{1v}^2 + c_{2v}^2 + 2c_{1v}c_{2v}\mathbf{e}_1 \cdot \mathbf{e}_2],$$

$$R_\psi = \pi\omega_v \mu_v^2 c_{1v}c_{2v}\mathbf{e}_1 \cdot \mathbf{r}_{C_1C_2} \times \mathbf{e}_2,$$

$$g = 4 R_\psi / D_\psi$$

where \mathbf{e}_1 and \mathbf{e}_2 are the unit vectors of C_1H_1 and C_2H_2 , $\mathbf{r}_{C_1C_2}$ is the oriented distance vector from C_1 to C_2 , and ω_v is the wavenumber of the considered transition. We have defined $\mu_v = (\partial\mu/\partial r)\langle 0|r|v\rangle + (\partial^2\mu/\partial r^2)\langle 0|r^2|v\rangle$ for both C_1H_1 and C_2H_2 . Let us now consider the quantities $R^* = R_\psi/(\mu_v^2)$ and $D^* = D_\psi/(\mu_v^2)$, which remove the contribution from μ_v^2 that varies from overtone to overtone. Let us consider case C of Table 1 and let us see whether these values allow one to interpret the results of Figure 1. From Ref. 3, we have $\mathbf{e}_1 \cdot \mathbf{e}_2 = 0.3333$ and $\mathbf{e}_1 \cdot \mathbf{r}_{C_1C_2} \times \mathbf{e}_2 = 1.1855 \text{ \AA}$. Thus:

for $\Delta v = 1$

| | |
|-----------------------------|----------------------------|
| at 2859 cm^{-1} | at 2904 cm^{-1} |
| $c_1 = 0.52$ | $c_1 = 0.85$ |
| $c_2 = -0.85$ | $c_2 = 0.52$ |
| $R^* = -0.47 \cdot 10^{-4}$ | $R^* = 0.48 \cdot 10^{-4}$ |
| $D^* = 0.70$ | $D^* = 1.29$ |
| $g = -2.7 \cdot 10^{-4}$ | $g = 1.49 \cdot 10^{-4}$ |

for $\Delta v = 2$

| | | |
|----------------------------|-----------------------------|----------------------------|
| at 5608 cm^{-1} | at 5666 cm^{-1} | at 5780 cm^{-1} |
| $c_1 = 0.08$ | $c_1 = 0.96$ | $c_1 = 0.17$ |
| $c_2 = 0.98$ | $c_2 = -0.12$ | $c_2 = 0.26$ |
| $R^* = 0.17 \cdot 10^{-4}$ | $R^* = -0.25 \cdot 10^{-4}$ | $R^* = 0.09 \cdot 10^{-4}$ |
| $D^* = 1.01$ | $D^* = 0.87$ | $D^* = 0.13$ |
| $g = 0.68 \cdot 10^{-4}$ | $g = -1.17 \cdot 10^{-4}$ | $g = 3.00 \cdot 10^{-4}$ |

for $\Delta v = 3$

| | | | |
|-----------------------------|----------------------------|-----------------------------|----------------------------|
| at 8220 cm^{-1} | at 8339 cm^{-1} | at 8492 cm^{-1} | at 8583 cm^{-1} |
| $c_1 = 0.01$ | $c_1 = 0.98$ | $c_1 = 0.12$ | $c_1 = 0.13$ |
| $c_2 = -0.99$ | $c_2 = 0.02$ | $c_2 = -0.11$ | $c_2 = 0.05$ |
| $R^* = -0.02 \cdot 10^{-4}$ | $R^* = 0.05 \cdot 10^{-4}$ | $R^* = -0.04 \cdot 10^{-4}$ | $R^* = 0.02 \cdot 10^{-4}$ |
| $D^* = 0.97$ | $D^* = 0.98$ | $D^* = 0.02$ | $D^* = 0.02$ |
| $g = -0.09 \cdot 10^{-4}$ | $g = 0.19 \cdot 10^{-4}$ | $g = -9.49 \cdot 10^{-4}$ | $g = 3.66 \cdot 10^{-4}$ |

for $\Delta v = 4$

| | | | | |
|-----------------------------|-------------------------------|----------------------------|-----------------------------|-----------------------------|
| at 10,702 cm^{-1} | at 10,901 cm^{-1} | at 11,116 cm^{-1} | at 11,211 cm^{-1} | at 11,338 cm^{-1} |
| $c_1 = 0.001$ | $c_1 = 0.99$ | $c_1 = 0.02$ | $c_1 = 0.12$ | $c_1 = 0.05$ |
| $c_2 = -1.00$ | $c_2 = -0.0001$ | $c_2 = 0.10$ | $c_2 = -0.02$ | $c_2 = 0.015$ |
| $R^* = -0.01 \cdot 10^{-4}$ | $R^* = -0.0003 \cdot 10^{-4}$ | $R^* = 0.01 \cdot 10^{-4}$ | $R^* = -0.01 \cdot 10^{-4}$ | $R^* = 0.003 \cdot 10^{-4}$ |
| $D^* = 1.00$ | $D^* = 0.98$ | $D^* = 0.01$ | $D^* = 0.01$ | $D^* = 0.003$ |
| $g = -0.02 \cdot 10^{-4}$ | $g = -0.001 \cdot 10^{-4}$ | $g = 3.48 \cdot 10^{-4}$ | $g = -2.92 \cdot 10^{-4}$ | $g = 4.10 \cdot 10^{-4}$ |

This simplified evaluation of R^* , D^* , and g gives results in good agreement with those presented in Figure 1 and Table 1, and thus we may understand that the absorption spectrum is dominated by the first two transitions in each overtone manifold ν , while the VCD spectrum has contribution at higher frequencies; the latter features may be detectable since they have favorable g factor (ca. 10^{-4}), unlike e.g. the first two lowest-frequency features at $\Delta\nu = 4$. However, their detection may be difficult due to the low absorption.

CONCLUSIONS

In this work we have established what is the general aspect of absorption and VCD spectra for fundamental ($\Delta\nu = 1$) and overtone CH-stretching transitions up to $\Delta\nu = 4$ for a general chiral HCCH fragment in the case of coupled dipole mechanism. In particular, for positive harmonic interaction constants K_{12} between the two CH-stretching vibrations a scheme of alternating signs in the predicted VCD spectra at successive $\Delta\nu$ values is expected, whereas a constant scheme is expected at successive $\Delta\nu$ values for negative K_{12} . We have also rationalized why the most intense absorption features do not necessarily coincide with the most intense VCD features. All of this can be appreciated by looking at Figures 1 and 2, which are derived for a particular choice of parameters' values; however the method is altogether general and the parameters can be changed if necessary.

We wish to make another couple of comments: we believe that a simple coupled-oscillator model of electric bond dipoles cannot be the only mechanism for generating VCD spectra associated with overtone transitions, unless an enhancement of effective interactions between bonds is present. An important contribution in generating magnetic dipole moments can be given by polarizable groups²⁷ or ring currents²⁸; for fundamental transitions such contributions and all others are encompassed by the general theory of vibrational circular dichroism by Stephens²⁹: these mechanisms may even explain high rotational strengths in case of local modes as found in Ref. 22. In any case we think that the first task in understanding overtone VCD spectra is the solution of the anharmonic dynamical problem with special attention to the eigenstates representing high-energy vibrations, and we believe that the present work sheds light onto this aspect.

Last but not least, we observe that the global aspect of Figures 1 and 2 could be arrived at also by a more standard variational approach (see, e.g., Ref. 18). Yet, we think that the Van Vleck-based approach, that has been applied a few times in papers regarding VCD,^{11,30,31} can find an easier implementation in packages allowing calculations of general properties, as done already for a particular molecular case by Bak et al.³² to treat anharmonicity in the standard IR region. For the CH-stretching overtone region the variant of Van Vleck contact transformation method in terms of raising and lowering operators, that has been developed by Sibert¹⁷ to interpret the absorption spectra and has been extended here to treat VCD, is thought to be necessary to make the problem computationally tractable.

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APPENDIX I

We report the coefficients of the studied Hamiltonian obtained from the mechanical parameters of two harmonically coupled Morse oscillators.

$$K_{+++} = -\frac{1}{\sqrt{2}} \frac{(\omega_{01}^2 \sqrt{\chi_1} \cos^3 \beta + \omega_{02}^2 \sqrt{\chi_2} \sin^3 \beta)}{\omega_+^{3/2}},$$

$$K_{---} = -\frac{1}{\sqrt{2}} \frac{(-\omega_{01}^2 \sqrt{\chi_1} \sin^3 \beta + \omega_{02}^2 \sqrt{\chi_2} \cos^3 \beta)}{\omega_-^{3/2}},$$

$$K_{++-} = -\frac{3}{\sqrt{2}} \frac{(-\omega_{01}^2 \sqrt{\chi_1} \cos \beta + \omega_{02}^2 \sqrt{\chi_2} \sin \beta) \sin \beta \cdot \cos \beta}{\sqrt{\omega_- \omega_+}},$$

$$K_{+--} = -\frac{3}{\sqrt{2}} \frac{(\omega_{01}^2 \sqrt{\chi_1} \sin \beta + \omega_{02}^2 \sqrt{\chi_2} \cos \beta) \sin \beta \cdot \cos \beta}{\sqrt{\omega_+ \omega_-}},$$

$$K_{++++} = \frac{7}{12} \frac{(\omega_{01}^2 \chi_1 \cos^4 \beta + \omega_{02}^2 \chi_2 \sin^4 \beta)}{\omega_+^2},$$

$$K_{----} = \frac{7}{12} \frac{(\omega_{01}^2 \chi_1 \sin^4 \beta + \omega_{02}^2 \chi_2 \cos^4 \beta)}{\omega_-^2},$$

$$K_{+---} = \frac{7}{2} \frac{(\omega_{01}^2 \chi_1 + \omega_{02}^2 \chi_2) \sin^2 \beta \cos^2 \beta}{\omega_+ \omega_-},$$

$$K_{++--} = \frac{7}{3} \frac{(-\omega_{01}^2 \chi_1 \cos^2 \beta + \omega_{02}^2 \chi_2 \sin^2 \beta) \sin \beta \cdot \cos \beta}{\sqrt{\omega_- \omega_+^3}},$$

$$K_{+---} = \frac{7}{3} \frac{(-\omega_{01}^2 \chi_1 \sin^2 \beta + \omega_{02}^2 \chi_2 \cos^2 \beta) \sin \beta \cdot \cos \beta}{\sqrt{\omega_+ \omega_-^3}},$$

where β is given by:

$$\beta = \frac{1}{2} \cos^{-1} \left(\frac{\omega_{01}^2 - \omega_{02}^2}{\sqrt{(\omega_{01}^2 - \omega_{02}^2)^2 + 4K_{12}^2 / (4\pi^2 c^2 m)^2}} \right).$$

β defines the normal modes as follows:

$$\Delta l_1 = \frac{q_+ \cos \beta - q_- \sin \beta}{\sqrt{m}},$$

$$\Delta l_2 = \frac{q_+ \cos \beta + q_- \sin \beta}{\sqrt{m}}$$

APPENDIX II

Here we wish to compare the twice transformed Hamiltonian $H^{(2)} = H_0 + H_2^{(2)}$ with the analogous dynamical

$$x_{13} = \frac{2K_{+--}^2 \omega_+ \omega_- - 3K_{+--} K_{+++} \omega_+^2 + 12K_{+--} K_{+++} \omega_-^2 + K_{+--} \omega_+^3 - 4K_{+++} \omega_+ \omega_-^2}{\omega_+ (\omega_+^2 - 4\omega_-^2)},$$

approximations proposed in the literature¹⁸ in terms of the raising and lowering operators. We follow the same notation of Ref. 18, i.e., #1 for the symmetric and #3 for the antisymmetric normal mode. The correspondence with our notation is:

$$A_1 = a_+; A_1^\dagger = a_+^\dagger; A_3 = a_-; A_3^\dagger = a_-^\dagger$$

We thus obtained

$$\begin{aligned} \frac{H}{hc} = & \omega_1 (A_1^\dagger A_1 + \frac{1}{2}) + \omega_3 (A_3^\dagger A_3 + \frac{1}{2}) \\ & + x_{11} (A_1^\dagger A_1 (A_1^\dagger A_1 + 1) + \frac{1}{4}) + x_{33} (A_3^\dagger A_3 (A_3^\dagger A_3 \\ & + 1) + \frac{1}{4}) + x_{13} (A_1^\dagger A_1 A_3^\dagger A_3 + \frac{1}{2} (A_1^\dagger A_1 + A_3^\dagger A_3 \\ & + \frac{1}{2}) + \frac{1}{4} K_{1133} (A_1^\dagger A_1^\dagger A_3 A_3 + A_3^\dagger A_3^\dagger A_1 A_1) T \\ & + K_{1113} (A_1^\dagger A_3 (1 + N_1) + (N_1 + 1) A_3^\dagger A_1) \\ & + K_{1333} (A_3^\dagger A_1 (1 + N_3) + (N_3 + 1) A_1^\dagger A_3), \end{aligned} \quad (A1)$$

where we have also introduced the number operators N_1 and N_3 for the symmetric and antisymmetric states, namely:

$$N_1 = A_1^\dagger A_1 \quad \text{and} \quad N_3 = A_3^\dagger A_3$$

Apart from the constant term T (see below) and the last two terms (with constants K_{1113} and K_{1333}), typical of different oscillators, Hamiltonian (A1) formally coincides with that of Halonen.¹⁸ The constant term T adds to the zero-point energy a term equal to

$$-\frac{3}{8} K_{++++} + \frac{7}{16} \frac{K_{+++}^2}{\omega_+} - \frac{3}{8} K_{--} + \frac{3}{16} \frac{K_{+-}^2 \omega_+}{(\omega_+^2 - 4\omega_-^2)}$$

which, assuming for the K coefficients a relationship typical of the Morse oscillator (and when the coupling constant vanishes), approaches $-(1/4)\chi$ (see Ref. 13).

All matrix elements generated by Eq. (A1) coincide with the ones given by Lehmann¹⁹ in a study of HCN and DCN.

We report here for completeness all of the constants of Eq. (A1):

$$x_{11} = \frac{3}{4} \frac{-5K_{+++}^2 + 2K_{++++}\omega_+}{\omega_+},$$

$$x_{33} = -\frac{1}{4} \frac{3K_{+--}^2 \omega_+^2 - 8K_{+--}^2 \omega_-^2 - 6K_{+--} \omega_+^3 + 24K_{+--} \omega_+ \omega_-^2}{\omega_+ (\omega_+^2 - 4\omega_-^2)},$$

$$K_{1133} = -\frac{2K_{+--}^2 \omega_- (\omega_+ + 2\omega_-)}{\omega_+ (\omega_+^2 - 4\omega_-^2)} - \frac{K_{+--} K_{+++} (\omega_+^2 + 2\omega_-^2)}{\omega_+ (\omega_+^2 - 4\omega_-^2)} + K_{+--},$$

$$K_{1113} = -\frac{1}{4} \frac{(29\omega^2 + \omega_- - 5\omega_+^3 + 6\omega_+^3) K_{+--} K_{+++}}{\omega_+ \omega_- (4\omega_+^2 - \omega_+^2)} - \frac{1}{4} \times \frac{(15\omega_+ \omega_-^4 - 8\omega_+^2 \omega_-^3 - 47\omega_+^3 \omega_-^2 + 8\omega_+^5 + 2\omega_-^5) K_{+--} K_{+++}}{\omega_+ \omega_- (4\omega_+^2 - \omega_-^2) (\omega_+^2 - 4\omega_-^2)} + \frac{3}{4} K_{++++},$$

$$K_{1333} = -\frac{1}{4} \frac{(29\omega^2 \omega_+ + 6\omega_-^3 - 5\omega_+^3) K_{+--} K_{+--}}{\omega_+ \omega_- (4\omega_-^2 - \omega_+^2)} - \frac{1}{4} \times \frac{(15\omega_+ \omega_-^4 - 8\omega_+^2 \omega_-^3 - 47\omega_+^3 \omega_-^2 + 8\omega_+^5 + 2\omega_-^5) K_{+--} K_{+--}}{\omega_+ \omega_- (4\omega_+^2 - \omega_-^2) (\omega_+^2 - 4\omega_-^2)} + \frac{3}{4} K_{+----}. \quad (A2)$$

Expressions (A2) hold for different oscillators; if they are alike, then Eqs. (A2) take up the form given by Halonen.¹⁸ The last two terms of Eq. (A1) with the K_{1113} and K_{1333} coefficients are related to the 1:1 resonance, as can be easily seen remembering the intrinsic property of the operators, which is to create and to destroy (vibrational) quanta in the oscillator they refer to. The presence of terms containing the number operator implies an amplification of the 1:1 resonance effect with increasing overtone order.

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