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# The vibrational circular dichroism of dimethylcyclopropane in the C–H stretching region

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The vibrational circular dichroism (VCD) of dimethylcyclopropane is studied by *ab initio* techniques. The equilibrium geometry, the molecular force field, and the matrix elements for the infrared (IR) and VCD intensities are evaluated using the derivative method for molecular wave functions of SCF type. An alternative derivation of Stephens' expression for the rotational strength is presented. The results are compared with the available experimental information for the C–H stretching modes. This is an excellent demonstration of the validity of this theory for the VCD intensity of the C–H vibrations, which are easily rationalized using group theoretical arguments.

## I. INTRODUCTION

There has been considerable interest in recent years on both the measurements and the theory for vibrational circular dichroism (VCD).<sup>1–3</sup> Since an earlier paper by Craig and Thirunamachandran<sup>4</sup> it has been recognized that a satisfactory interpretation of VCD intensities requires the explicit description of the molecular electronic structure and the inclusion of corrections for the nuclear motion.

An important recent contribution in the field is due to Stephens,<sup>5</sup> who has reformulated the problem to obtain a closed analytical expression for the vibronic contributions to VCD. We note that this formula was also derived independently by Galwas.<sup>6,8</sup> By extending the concept of the property surface<sup>7</sup> to include the case of velocity dependent properties, a novel interpretation of VCD has been given.<sup>8,9</sup> This makes more transparent the connection with the atomic tensors expressing the variation of the electric fields at the nuclear sites in the presence of the radiation field.<sup>10,11</sup>

Stephens formula has been in fact successfully implemented using the SCF approximation for the electronic molecular wave functions.<sup>12,15,18</sup> The results of the first few applications to simple chiral molecules have indicated the utility of the approach for the interpretation of VCD spectral data.<sup>12,13,15–18</sup>

In this paper we first present a matrix formulation of the derivation of Stephens' formula. We then describe the application of the method to predict VCD intensities of *trans*-dimethylcyclopropane. Compared to previous studies of similar molecules, the complexity of the problem is somewhat increased, due to the increased number of internal degrees of freedom. On the other hand, the overall symmetry, the absence of molecular flexibility and conformational isomerism makes this molecule an ideal candidate for experimental and theoretical studies of VCD.

The results obtained confirm the great importance of the vibronic contributions to VCD and are found to be in satisfactory agreement with the available VCD data. More-

over these are easily rationalized using group theoretical arguments as discussed in the final section of this paper.

## II. THEORY

In this section, we give an alternative derivation of Stephens formula. Unlike Stephens we shall not assume that exact eigenfunctions of the Born–Oppenheimer (BO) are known, but start from a matrix representation of the problem, which is nearer to practical calculation. An approximation to the formula is also derived, which may be found useful when, for molecular wave functions of general form, the required wave function derivatives<sup>5</sup> are not easily obtained.

We start by defining the molecular Hamiltonian

$$H(q, Q) = T_N(Q) + H_e(q, Q). \quad (1)$$

For simplicity, we restrict the nuclear motion to a single normal mode  $Q$  and write the corresponding contribution to the nuclear kinetic energy operator in atomic units as

$$T_N(Q) = -\frac{1}{2} \frac{\partial^2}{\partial Q^2}. \quad (2)$$

$H_e(q, Q)$  is the electronic Hamiltonian inclusive of the nuclear repulsion energy term,  $q$  being the set of the electronic variables. We use a basis of real vibronic wave functions

$$\{\Phi_I(q, Q)\chi_k(Q)\}, \quad (3)$$

where  $I$  and  $k$  are collective electronic and vibrational quantum numbers, respectively, to build the approximate eigenfunctions of the full vibronic Hamiltonian (1). There are, in fact, two possible convenient choices for the electronic factors: adiabatic factors  $\Phi_I(q, Q)$  chosen to make diagonal the electronic Hamiltonian matrix

$$\langle \Phi_I(q, Q) | H_e(q, Q) | \Phi_J(q, Q) \rangle_q = \delta_{IJ} E_I^q \quad (4)$$

at any value of the nuclear coordinate  $Q$  or electronic factors  $\Phi_I^0(q, 0)$ , for which Eq. (4) applies only at a given reference geometry, where the value of the internal coordinate  $Q$  is set to zero

$$\langle \Phi_I^0(\mathbf{q}, 0) | \mathbf{H}_e(\mathbf{q}, 0) | \Phi_J^0(\mathbf{q}, 0) \rangle_{\mathbf{q}} = \delta_{IJ} E_I^0. \quad (5)$$

This latter choice will be referred to as the crude adiabatic (CA) approximation, though in fact the model is not used in its strictest form, as will be explained later. Harmonic vibrational factors  $\chi_k$  are most commonly used to build the vibronic basis (3).

For sake of completeness, using equalities (4) and (5), we write the matrix elements of the full Hamiltonian

$$H_{Ik,Jl} = \langle \chi_k \langle \Phi_I | \mathbf{H} | \Phi_J \rangle_{\mathbf{q}} \chi_l \rangle_Q. \quad (6)$$

Integration over the nuclear coordinate  $Q$ , following the integration over the electronic variables  $\mathbf{q}$ , enables the matrix element (6) to be written in the adiabatic basis

$$H_{Ik,I} = \langle \chi_k | \mathbf{T}_N + E_I^0 | \chi_l \rangle_Q - \frac{1}{2} \left\langle \chi_k \langle \Phi_I | \frac{\partial^2}{\partial Q^2} | \Phi_I \rangle_{\mathbf{q}} \chi_l \right\rangle_Q, \quad (7a)$$

$$H_{Ik,Jl} = -\frac{1}{2} \left\langle \chi_k \langle \Phi_I | \frac{\partial^2}{\partial Q^2} | \Phi_J \rangle_{\mathbf{q}} \chi_l \right\rangle_Q - \left\langle \chi_k \langle \Phi_I | \frac{\partial}{\partial Q} | \Phi_J \rangle_{\mathbf{q}} \frac{\partial}{\partial Q} \chi_l \right\rangle_Q \quad (I \neq J) \quad (7b)$$

and in the CA basis

$$H_{Ik,I} = \langle \chi_k | \mathbf{T}_N | \chi_l \rangle_Q + \langle \chi_k \langle \Phi_I^0 | \mathbf{H}_e(\mathbf{q}, Q) | \Phi_I^0 \rangle_{\mathbf{q}} \chi_l \rangle_Q, \quad (8a)$$

$$H_{Ik,Jl} = \langle \chi_k \langle \Phi_I^0 | \mathbf{H}_e(\mathbf{q}, Q) | \Phi_J^0 \rangle_{\mathbf{q}} \chi_l \rangle_Q \quad (I \neq J). \quad (8b)$$

The diagonal ( $I = J$ ) blocks of the Hamiltonian matrix are generated from Eq. (7a) or (8a) and the off-diagonal blocks ( $I \neq J$ ) from Eq. (7b) or (8b). We shall further assume that in Eqs. (7a) and (7b) the terms involving the second derivatives of the adiabatic electronic factors ( $\partial^2 \Phi_I / \partial Q^2$ ) are negligible compared to the remaining terms.

A polynomial approximation to the electric Hamiltonian  $\mathbf{H}_e$

$$\mathbf{H}_e(\mathbf{q}, Q) = \mathbf{H}_e(\mathbf{q}, 0) + \left( \frac{\partial \mathbf{H}_e}{\partial Q} \right)_0 Q + \frac{1}{2} \left( \frac{\partial^2 \mathbf{H}_e}{\partial Q^2} \right)_0 Q^2 + \dots \quad (9)$$

provides the explicit dependence of the operator on the nuclear coordinate, giving, in the CA basis, factorized expressions for the matrix elements, i.e., for the off-diagonal blocks

$$H_{Ik,Jl} = \langle \Phi_I^0 | \left( \frac{\partial \mathbf{H}_e}{\partial Q} \right)_0 | \Phi_J^0 \rangle_{\mathbf{q}} \langle \chi_k | Q | \chi_l \rangle_Q + \dots \quad (10)$$

The Hamiltonian matrix (6) may be decomposed into a block-diagonal component  $\mathbf{H}_0^{\text{vib}}$  and its complement  $\mathbf{h}$

$$\mathbf{H} = \mathbf{H}_0^{\text{vib}} + \mathbf{h}, \quad (11)$$

where  $H_{0Ik,I}^{\text{vib}}$  is defined by Eq. (7a) for the adiabatic basis and by Eq. (8a) for the CA basis.  $\mathbf{H}_0^{\text{vib}}$  is further split into the diagonal matrix  $\mathbf{H}_0$  and the shifted vibrational Hamiltonian  $\mathbf{H}^{\text{vib}}$ , providing, respectively, the electronic origins  $E_I^0$  and the corresponding relative vibronic energies  $\hbar\omega_I^I$

$$\mathbf{H}_0^{\text{vib}} = \mathbf{H}_0 + \mathbf{H}^{\text{vib}}. \quad (12)$$

In a variation perturbation treatment, the  $\mathbf{h}$  matrix, including all off-diagonal blocks of the Hamiltonian matrix,

will be treated as a perturbation and we write the zero order equation as

$$[(\mathbf{H}_0 + \mathbf{H}^{\text{vib}}) - (E_I^0 + \hbar\omega_I^I) \mathbf{1}] C_I^I = 0, \quad (13)$$

where  $C_I^I$  represents the vibronic wave function  $\sum_l C_{Il}^I \Phi_l \chi_l$ . The vibronic factors are not the same in the adiabatic and CA models as the matrix elements are not the same. However in practice most calculations have used harmonic factors, regardless of the route by which the equations have been derived. Given the definition of the matrices in Eqs. (11)–(13), the resulting wave function represented by  $C_I^I$  is a BO approximation to the molecular vibronic wave function and therefore unable to describe the electronic relaxation after a vibrational excitation. One of the consequences, is that the electron contribution to the magnetic dipole of any vibrational excitation is identically zero in this approximation

$$\mathbf{m}_{eij}^{\beta} = \mathbf{C}_I^{\dagger} \mathbf{m}_e^{\beta} \mathbf{C}_I^I. \quad (14)$$

The latter quantity plays an important role in the analysis of vibrational circular dichroism spectra, since the dichroism of a vibrational transition is related to its rotational strength

$$R_{ij} = \Im(\mathbf{d}_{ij} \cdot \mathbf{m}_{ij}), \quad (15)$$

$\mathbf{d}_{ij}$  being the electric dipole of the transition. The inclusion of the vibronic perturbation matrix elements  $\mathbf{h}$ , providing the coupling with the excited electronic factors  $\Phi_K$  ( $K \neq I$ ), becomes essential for the theoretical prediction of VCD intensities. The resulting wave function, by allowing the simultaneous excitation of vibrational and electronic states, is able to correlate the motion of the electrons to the nuclei vibration.

With the inclusion of the vibronic effects, the electron contribution to the magnetic dipole for a vibrational transition, becomes

$$\mathbf{m}_{eij}^{\beta} = \delta \mathbf{C}_I^{\dagger} \mathbf{m}_e^{\beta} \mathbf{C}_I^I + \mathbf{C}_I^{\dagger} \mathbf{m}_e^{\beta} \delta \mathbf{C}_I^I, \quad (16)$$

where the structure of the various matrices is shown in Fig. 1 and the correction to the BO wave function is obtained by first order perturbation theory

$$\mathbf{H}^0 = \begin{vmatrix} E_I^0 \mathbf{1}_I & 0 \\ 0 & E_J^0 \mathbf{1}_J \end{vmatrix} \quad \mathbf{H}^{\text{vib}} = \begin{vmatrix} \mathbf{H}_I^{\text{vib}} & 0 \\ 0 & \mathbf{H}_J^{\text{vib}} \end{vmatrix}$$

$$\mathbf{h} = \begin{vmatrix} 0 & \mathbf{h}_{IJ} \\ \tilde{\mathbf{h}}_{JI} & 0 \end{vmatrix} \quad \mathbf{m}^{\beta} = \begin{vmatrix} 0 & \mathbf{m}_{IJ}^{\beta} \\ -\tilde{\mathbf{m}}_{JI}^{\beta} & 0 \end{vmatrix}$$

FIG. 1. Matrices determining the vibronic contributions to the VCD intensity, for a nontotally symmetric vibrational coordinate.

$$\delta C_I^i = -[\mathbf{H}_0 + \mathbf{H}^{\text{vib}} - (E_I^0 + \hbar\omega_I^i)\mathbf{1}]^{-1}\mathbf{h}C_I^i. \quad (17)$$

By expanding the resolvent operator, an expression is obtained for the transition magnetic dipole involving a full summation over all excited molecular states.<sup>4</sup>

Stephens has recently reconsidered the problem using a similar approach but reducing the final expression to a closed analytic formula involving derivatives of the molecular wave functions.<sup>5</sup> To this purpose Eq. (17) is rewritten as

$$\begin{aligned} \delta C_I^i = & -(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}\mathbf{h}C_I^i + (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \\ & \times (\mathbf{H}^{\text{vib}} - \hbar\omega_I^i\mathbf{1})(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}\mathbf{h}C_I^i \\ & - (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}(\mathbf{H}^{\text{vib}} - \hbar\omega_I^i\mathbf{1})(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \\ & \times (\mathbf{H}^{\text{vib}} - \hbar\omega_I^i\mathbf{1})(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}\mathbf{h}C_I^i. \end{aligned} \quad (18)$$

The first term on the right-hand side of Eq. (18) generates nonzero contributions to both terms in Eq. (16) whose order of magnitude is given by the ratio between a typical vibrational and electronic excitation energy. However the two terms sum to zero due to the Hermitian nature of the complex operator  $\mathbf{m}_e^\beta$  and the structure of the  $\mathbf{H}_0$  matrix, whose diagonal elements depend only on the electronic quantum numbers  $I$  (see Fig. 1). The second term in Eq. (18) varies with the degree of vibrational excitation and gives nonvanishing contributions to the magnetic dipole. Their order of magnitude is approximately the square of the previous quantities. The next higher order terms in the expansion (18) are one order of magnitude lower and can be safely neglected at the present level of approximation. Therefore using the second term of Eq. (18), the magnetic dipole expression (16), consists of the following contributions

$$-\hbar\omega_I^i C_I^{\dagger} \mathbf{h}^{\dagger} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-2} \mathbf{m}_e^\beta C_I^j, \quad (19a)$$

$$-\hbar\omega_I^j C_I^{\dagger} \mathbf{m}_e^{\beta\dagger} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-2} \mathbf{h} C_I^j, \quad (19b)$$

$$C_I^{\dagger} \mathbf{h}^{\dagger} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \mathbf{H}^{\text{vib}} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \mathbf{m}_e^\beta C_I^j, \quad (19c)$$

$$C_I^{\dagger} \mathbf{m}_e^{\beta\dagger} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \mathbf{H}^{\text{vib}} (\mathbf{H}_0 - E_I^0\mathbf{1})^{-1} \mathbf{h} C_I^j. \quad (19d)$$

Equations (19a)–(19d) can be easily generalized to include the case of nonorthogonal sets of vibrational factors  $\{\chi\}$ .

Assuming a complete set of vibrational expansion functions, the sum of the first two terms Eq. (19a), Eq. (19b) is easily obtained to give

$$\begin{aligned} (19a) + (19b) = & -\hbar(\omega_I^j - \omega_I^i) C_I^{\dagger} \mathbf{m}_e^{\beta\dagger} \\ & \times (\mathbf{H}_0 - E_I^0\mathbf{1})^{-2} \mathbf{h} C_I^j. \end{aligned} \quad (20)$$

A similar simplification of Eqs. (19c) and (19d) terms, is not possible since the matrix elements of the “intermediate” vibrational Hamiltonian  $\mathbf{H}^{\text{vib}}$ , will depend in general on the electronic  $I$  and vibrational  $i$  quantum numbers.

Equations (20), (19c), and (19d) can be regarded as “scalar products” involving vectors of the type

$$-(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}\mathbf{h}C_I^j, \quad (21a)$$

$$(\mathbf{H}_0 - E_I^0\mathbf{1})^{-1}\mathbf{m}_e^\beta C_I^i. \quad (21b)$$

Equation (21a) is the first order vibronic correction to the BO state ( $Ij$ ). The perturbation matrix  $\mathbf{h}$  consists of the off-diagonal elements (7b) or (8b). For the CA case, which we discuss first, the vibronic operator  $\mathbf{h}$  is approximated as  $(\partial\mathbf{H}_e/\partial Q)_0 Q$  [the second term in Eq. (9)], to take into

account the adiabatic vibronic interactions.<sup>19</sup> Therefore, each component of the “vibronic vector” (21a) is written

$$\begin{aligned} \sum_k & -(E_k^0 - E_I^0)^{-1} |\Phi_k^0 \chi_k\rangle \\ & \times \left\langle \chi_k \langle \Phi_k^0 | \left( \frac{\partial \mathbf{H}_e}{\partial Q} \right)_0 | \Phi_I^0 \rangle_a Q \chi_I \right\rangle_Q. \end{aligned} \quad (22)$$

Using the completeness identity  $\sum_k |\chi_k\rangle \langle \chi_k| = \mathbf{1}$ , Eq. (22) is transformed to

$$\sum_k -(E_k^0 - E_I^0)^{-1} |\Phi_k^0\rangle \langle \Phi_k^0| \left( \frac{\partial \mathbf{H}_e}{\partial Q} \right)_0 | \Phi_I^0 \rangle_a Q \chi_I \rangle \quad (23)$$

and Eq. (21a) rewritten as

$$\left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 Q \otimes \{\chi\} \right\rangle C_I^j \equiv \sum_k \left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 Q \chi_k \right\rangle C_{I_k}^j. \quad (24)$$

Similarly, the factor (21b) is the first order correction to the BO state ( $Ii$ ) due to a perturbing homogeneous magnetic field

$$-\left| \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \otimes \{\chi\} \right\rangle C_I^i. \quad (25)$$

It is worth asking whether the identification of Eq. (23) as the derivative of the wave function is consistent with the CA approximation. The quantities involved are all energies and wave functions calculated at the equilibrium geometry, however, in its original and strictest form<sup>47</sup> the CA approximation takes the electronic wave function to be constant everywhere and therefore there is no derivative. The use of Eq. (24) is thus an extension to the CA approximation, requiring that not just the electronic energies and wave functions, but also the derivative of the electronic wave function, coincide with the equivalent adiabatic functions at the reference geometry. In fact a sequence of corrections exist<sup>48</sup> which recovers the adiabatic expressions from the crude adiabatic factors. The equations (23) and (24) are also standard expressions from Herzberg–Teller perturbation theory.<sup>19</sup>

Equations equivalent to Eqs. (24) and (25) can also be obtained within the adiabatic expansion. The expression corresponding to Eq. (22) is

$$\sum_k -(E_k^0 - E_I^0)^{-1} |\Phi_k \chi_k\rangle \left\langle \chi_k \langle \Phi_k | \frac{\partial}{\partial Q} | \Phi_I \rangle_a \frac{\partial}{\partial Q} \chi_I \right\rangle_Q. \quad (22a)$$

To simplify this it is necessary to use the commutation relationship  $[\mathbf{Q}, \mathbf{H}] = \partial/\partial Q$ , and also to adopt the Condon approximation, ignoring the dependence of the electronic matrix elements upon  $Q$  and replacing them with their values at the reference geometry. If this is done then equations of the same form as Eqs. (24) and (25) are obtained, containing the same electronic factors, though the vibrational factors are, in principle, different.

By using Eqs. (24) and (25) we rewrite the vibronic contributions to the magnetic dipole (20), (19c), and (19d) as

$$-\hbar(\omega_I' - \omega_I'') \mathbf{C}_I^{\dagger} \left\langle \{\chi\} \otimes \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \otimes \{\chi\} \right\rangle_Q \mathbf{C}_I^j, \quad (26a)$$

$$\mathbf{C}_I^{\dagger} \left\langle \{\chi\} \otimes \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \mathbf{H}^{\text{vib}} \right| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \otimes \{\chi\} \right\rangle_Q \mathbf{C}_I^j, \quad (26b)$$

$$\mathbf{C}_I^{\dagger} \left\langle \{\chi\} \otimes \left\langle \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \left| \mathbf{H}^{\text{vib}} \right| \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \right\rangle_Q \otimes \{\chi\} \right\rangle_Q \mathbf{C}_I^j, \quad (26c)$$

where the  $\mathbf{H}^{\text{vib}}$  operator is defined through its matrix elements [see Eqs. (7a) or (8a) and (12)]. Equation (26a), by avoiding the expansion of the vibronic components of the molecular wave function over all excited molecular states has formally the advantage of defining the first contribution to the vibrational dichroism as a ground state molecular property. From the practical point of view, Eq. (26a) can be more easily implemented for theoretical prediction of VCD intensities, since molecular wave function derivatives are now routinely evaluated to obtain equilibrium and transition molecular geometries and properties.<sup>20</sup> Unfortunately this does not apply to the terms (26b) and (26c) unless further approximations are made, as besides an explicit expansion over electronic excited states require the knowledge of the corresponding BO adiabatic or CA potentials, since even in the CA case the matrix elements of  $\mathbf{H}^{\text{vib}}$  are functions of  $Q$ .

Taking the CA case first, if the Hamiltonian operator is expanded as a power series, and truncated at low order, then Eqs. (26a) + (26b) give

$$(26a) + (26b) = -\hbar(\omega_I' - \omega_I'') \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \times \mathbf{C}_I^{\dagger} \langle \{\chi\} | Q | \{\chi\} \rangle_Q \mathbf{C}_I^j, \quad (27a)$$

$$-\hbar(\omega_I' - \omega_I'') \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \left( \frac{\partial H_e}{\partial Q} \right)_0 \right| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \times \mathbf{C}_I^{\dagger} \langle \{\chi\} | Q^2 | \{\chi\} \rangle_Q \mathbf{C}_I^j + \text{higher terms}. \quad (27b)$$

This requires that the vibrational basis  $\chi$  forms a complete orthonormal set, but not that the vibrational wave function is harmonic. If it is not harmonic then both of these terms contribute to the VCD of the fundamental. If, however, a harmonic approximation is adopted then only Eq. (27a), which is equal to Eq. (26a), contributes and the total vibronic magnetic dipole is

$$m_{e_g}^\beta = -2\hbar(\omega_I' - \omega_I'') \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \langle \chi | Q | \chi \rangle \quad (28)$$

which is Stephens expression. If it is specifically wished to investigate anharmonic effects then the term (27b) is not the only contribution. However, one advantage of the present approach is that it is clearly possible, by returning to Eq. (9) and including all terms in  $Q^2$  throughout, to derive the appropriate expressions.

Returning to the adiabatic formalism a simplified expression for the vibronic contributions to the magnetic transition dipole (19c) and (19d) is recovered, if one, be-

sides neglecting the variation with the nuclear coordinate  $Q$  of the magnetic dipole matrix elements (i.e., the Condon approximation)

$$\langle \chi_k | \langle \Phi_I | \mathbf{m}_e^\beta | \Phi_J \rangle_Q | \chi_l \rangle_Q = \langle \Phi_I | \mathbf{m}_e^\beta | \Phi_J \rangle_Q \delta_{kl} \quad (29)$$

assumes identical vibronic wave functions for the ground and for the excited electronic states

$$\begin{aligned} \mathbf{C}_K^i &= \mathbf{C}_I^i \\ \omega_K^i &= \omega_I^i. \end{aligned} \quad (30)$$

Under these assumptions the following equality is easily proved

$$(19a) + (19b) = (19c) + (19d) \quad (31)$$

giving the simplified expression for the vibronic magnetic dipole

$$m_{e_g}^\beta = -2\hbar(\omega_I' - \omega_I'') \mathbf{C}_I^{\dagger} \mathbf{m}_e^\beta (\mathbf{H}_0 - E_I^0 \mathbf{1})^{-2} \mathbf{h} \mathbf{C}_I^j. \quad (32)$$

Alternatively, and presumably equivalent, if one starts from Eqs. (26a)–(26c) with the matrix elements defined in their adiabatic forms, and systematically applies the Condon approximation the Stephens expression (28) is again obtained.

The present derivation has started from a matrix formalism of the problem, which differs from previous investigations. Not surprisingly, if the same approximations are made, then the same final equation (28) is obtained. The derivation in Ref. 8 has features in common with the route called “crude adiabatic” here, whereas that in Ref. 5 is closer to the adiabatic route. The principal simplifying technique in both cases is to expand the wave functions, Hamiltonian, or matrix elements about a reference geometry and truncate the series at low order. Another approximation used in all cases is that the energy differences, e.g., in Eq. (22) are electronic rather than vibronic energies. This is an essential approximation as unless this is made the expressions do not factorize into products of electronic and vibrational terms. The harmonic approximation is also necessary to obtain Eq. (28). Alternative definitions of the magnetic dipole operator<sup>21</sup> to minimize the problems connected with the choice of the gauge<sup>22</sup> can be included in this formalism. The equations (19) are however more general and may be of use in circumstances where the approximations used to derive Eq. (28) are less valid, particularly where interactions between states are large, or anharmonic effects are very important. From the computational point of view, the closed formula (28) has clear advantages when the nuclear vibrational motion couples the ground to a large number of excited electronic states having similar potential energy profiles along the  $Q$  coordinate and when the Condon approximation holds. When on the contrary, the vibronic correction to the wave function is determined by a reduced number of dominant electronic interactions, the matrix formulation [Eqs. (20), (19c), and (19d)] provides a more convenient framework to account for large changes in the potential energy expression upon electron excitation and for large higher order contributions to the electric and to the magnetic transition moments. The matrix formalism would also be more convenient to describe

VCD effects occurring in the vibrational structure associated with an electronic transition.

When electronic wave functions of more general type than SCF are available and the wave function derivatives are not easily obtained or for very large chiral molecules, a simplified expression of the factor  $\langle (\partial\Phi_I/\partial H_\beta)_0 | (\partial\Phi_I/\partial Q)_0 \rangle_q$  in Eq. (31) is desirable. To this purpose, by averaging all excitation energies to a constant value  $\Delta E$ ,<sup>23-25</sup> the resolvent operator in Eq. (31) is approximated to a diagonal constant matrix reducing the factor to a single term expression

$$\begin{aligned} & \left\langle \left( \frac{\partial\Phi_I}{\partial H_\beta} \right)_0 \middle| \left( \frac{\partial\Phi_I}{\partial Q} \right)_0 \right\rangle_q \\ &= \sum_K (E_K^0 - E_I^0)^{-1} \langle \Phi_I | \mathbf{m}_\beta | \Phi_K \rangle_q \left\langle \Phi_K \middle| \frac{\partial\Phi_I}{\partial Q} \right\rangle_q \\ &\approx \Delta E^{-1} \sum_K \langle \Phi_I | \mathbf{m}_\beta | \Phi_K \rangle_q \left\langle \Phi_K \middle| \frac{\partial\Phi_I}{\partial Q} \right\rangle_q \\ &= \Delta E^{-1} \left\langle \Phi_I \middle| \mathbf{m}_\beta \middle| \frac{\partial\Phi_I}{\partial Q} \right\rangle_q. \end{aligned} \quad (33)$$

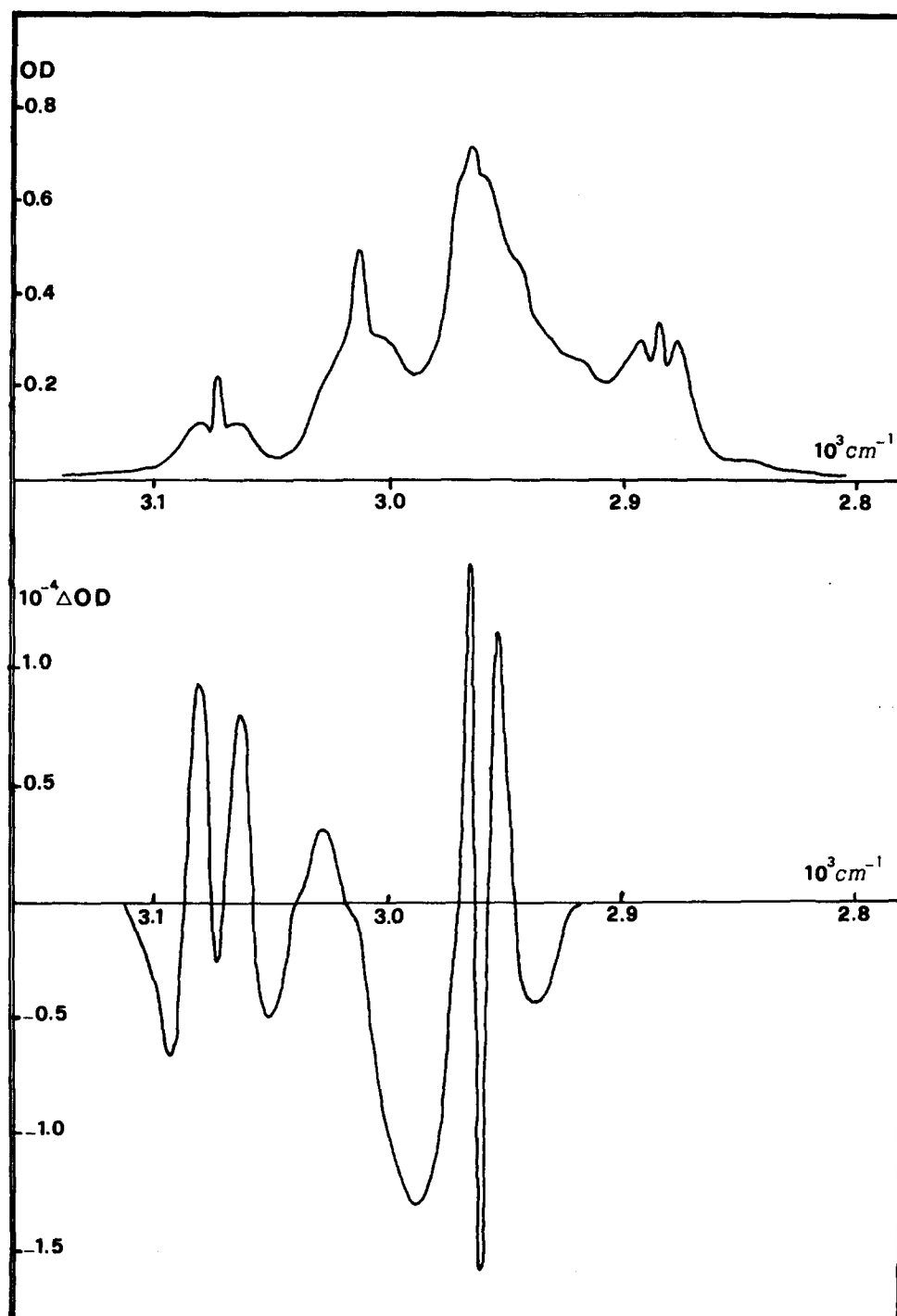


FIG. 2. Gas phase IR (upper) and VCD (lower) spectra of (2R,3R)-*trans* dimethylcyclopropane in the frequency range 2800–3100  $\text{cm}^{-1}$ ; IR optical densities (OD) and VCD density differences ( $\Delta OD$ ). CD spectral bandwidth  $\approx 3.5 \text{ cm}^{-1}$ .

This is easily evaluated by a finite difference method using molecular wave functions computed at the equilibrium  $\Phi_I^0$  and at a displaced geometry  $\Phi_I^Q$ , i.e., the internal coordinate value equal to  $Q$ ,

$$\begin{aligned} & \left\langle \left( \frac{\partial \Phi_I}{\partial H_\beta} \right)_0 \left| \left( \frac{\partial \Phi_I}{\partial Q} \right)_0 \right\rangle_Q \right. \\ & \approx (Q\Delta E)^{-1} \langle \Phi_I^0 | \mathbf{m}_\beta | \Phi_I^Q - \Phi_I^0 \rangle_Q \\ & = (Q\Delta E)^{-1} \langle \Phi_I^0 | \mathbf{m}_\beta | \Phi_I^Q \rangle_Q. \end{aligned} \quad (34)$$

Since for ground electronic states all excitation energies are positive, the average excitation energy approximation preserves the sign of all contributions to Eq. (33). When the selection or the propensity rules for the operators  $\mathbf{m}_\beta \partial / \partial Q$  are strict enough to concentrate the most important contributions to Eq. (33) in a short range of the energy spectrum, a judicious choice of the average excitation energy  $\Delta E$ , is likely to provide vibronic transition dipoles with correct signs and absolute values. The formula (33) is however an additional approximation which is only likely to be useful when examining a few particular vibrations in a large molecule.

### III. THE INTENSITY AND THE DICHROISM OF C-H VIBRATIONS

The IR and the VCD spectra of *trans*-dimethylcyclopropane in the vapor and in  $\text{CCl}_4$  solution have been recorded in the spectral range  $2800\text{--}3100\text{ cm}^{-1}$ . A complete description of the VCD spectrometer at Birbeck College has been given elsewhere.<sup>3,26</sup> It has a large area InSb detector and contains no mirror optics outside the monochromator. Under these conditions in the  $4000\text{--}2000\text{ cm}^{-1}$  region, artefactual CD signals are not observed and base lines are straight at the required sensitivity level. Solutions of cyclohexane in  $\text{CCl}_4$  at a concentration to mimic the dimethylcyclopropane absorption do not display dichroism. The gas phase spectra were obtained under an ambient nitrogen atmosphere in a 1 cm infrasil cell fitted with a Teflon stopper. The relative intensity of CD and absorption in the gas phase was independent of the amount of gaseous sample.

The (2*R*-3*R*)-dimethylcyclopropane was a gift from Professor L. Crombie. The preparation and the electron CD properties have been described.<sup>27</sup>

Here we summarize only those features of the spectra, which are relevant to the following discussion. In the spectral range investigated, the IR spectrum consists of four main absorption systems in the gas phase with centers at  $2880$ ,  $2960$ ,  $3010$ , and  $3070\text{ cm}^{-1}$ . In solution, three extra components are clearly observed to the low energy side of the  $2960\text{ cm}^{-1}$  envelope. The VCD spectrum of the  $2880\text{ cm}^{-1}$  absorption has vanishing optical activity in the gas phase but a small bisignate couplet is developed in solution. The  $2960\text{ cm}^{-1}$  envelope encompasses a strong fine structured pattern of alternating signs, which collapses to a single positive CD in solution. The well defined fine structure, which is observed under the highest energy absorption around  $3070\text{ cm}^{-1}$ , is clearly related to the rotational envelope of the band. This also collapses in solution. The  $3010\text{ cm}^{-1}$  absorption covers two VCD bands of opposite sign, which are clearly centered at  $3000\text{ cm}^{-1}$  in solution.

Gas phase and solution IR and VCD spectra of the (2*R*-3*R*) enantiomeric form, are shown in Figs. 2 and 3, respectively.

### IV. THEORETICAL RESULTS

Given an approximate molecular wave function, the evaluation of VCD intensities, by using Eq. (31), goes through the following steps. After the molecular equilibrium geometry ( $R_e$ ) has been determined, the wave function derivatives  $(\partial \Phi_I / \partial Q)_0$  with respect to all nuclear coordinates are evaluated. These provide one of the factors in Eq. (31). The mass weighted second derivative energy matrix is diagonalized to give normal vibrational coordinates. First order perturbation theory is also applied to obtain the remaining factor in the expression (31) for the rotational strengths, i.e., the magnetic perturbation to the wave function  $(\partial \Phi_I / \partial H_\beta)$ .

As discussed in the following sections these have been obtained for *trans*-dimethylcyclopropane using SCF molecular wave functions and 6-31G\* atomic orbitals.<sup>28,29</sup> These orbitals provide reasonable molecular geometries and reasonable predictions for the vibrational properties. A preliminary computation of the molecular geometry, vibrational frequencies, and VCD intensities was also performed with a reduced basis set of 3-21G orbitals.<sup>30</sup> The two sets of results

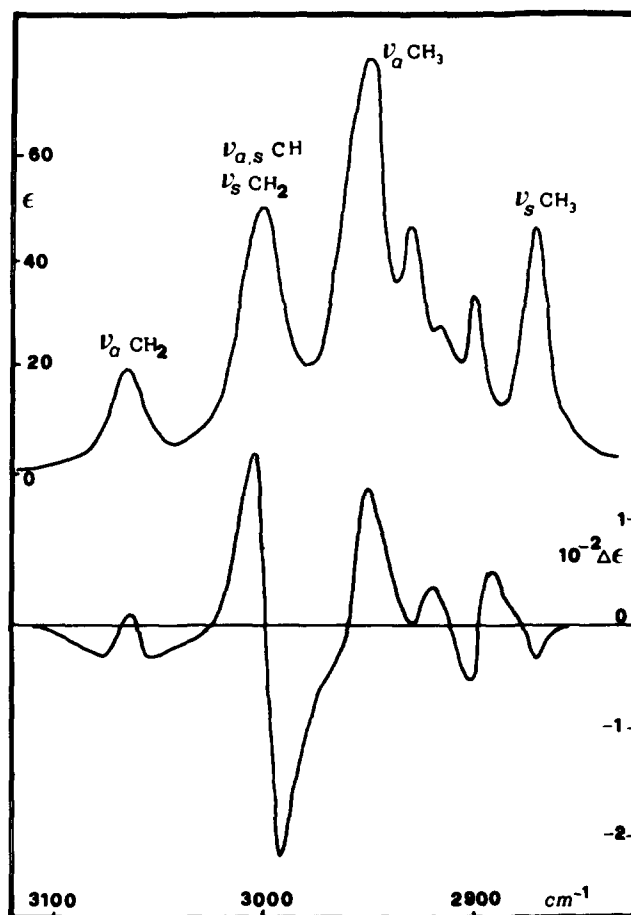


FIG. 3. IR and VCD  $\text{CCl}_4$  solution spectra of (2*R*-3*R*)-*trans*-dimethylcyclopropane. Proposed assignments for the  $\text{CH}_2$ , CH,  $\text{CH}_3$  symmetric ( $\nu_s$ ) and antisymmetric ( $\nu_a$ ) stretching vibrations.

have been compared to test the stability of our results with respect to changes in the atomic basis.

The computed equilibrium geometry is given in Table I. Only the CH stretching frequencies and intensities are required to discuss the IR and VCD spectra in Figs. 2 and 3 but the results for all frequencies are summarized in Table II.

### A. Molecular geometry

2,3-Dimethylcyclopropane can exist in two diastereoisomeric *trans* forms (2S-3S) and (2R-3R) and one optically inactive meso (*cis*) form. Computations were performed on the (2R-3R) optically active form shown in Fig. 4.

In Table I the computed equilibrium geometry is compared to the experimental geometry as determined from the electron diffraction study of Ref. 31. The two methyl groups are predicted to be staggered with respect to the ring hydrogens. The ring geometry is found to be a slightly distorted equilateral triangle and the C–C exocyclic bond considerably longer than the average C–C ring bond length. These aspects agree with the molecular model used to interpret electron diffraction data<sup>31</sup> and differ with previous theoretical estimates by Boggs *et al.*,<sup>32</sup> who, using a smaller basis set, predicted the exocyclic C–C bond length to be shorter than the ring C–C equilibrium bond distances. The assumption made in the study of the methyl internal rotation in methyl-

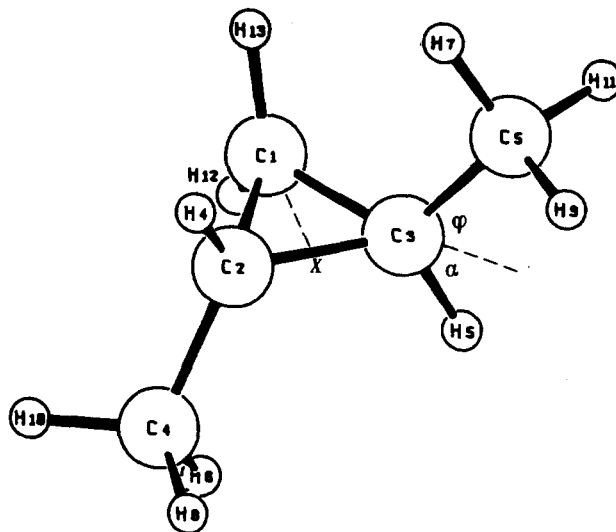


FIG. 4. Geometry and atomic indexes for (2R-3R)-*trans*-dimethylcyclopropane.

cyclopropane by microwave spectroscopy<sup>33</sup> of a C–CH<sub>3</sub> bond length which is slightly short relative to propane, is also not supported by the present results.

### B. Harmonic frequencies, normal modes, and VCD intensities

The only extensive tabulation of IR and Raman frequencies available in the literature for this molecule is due to Durig.<sup>34</sup> The molecular vibrations have been classified as (a) methyl torsions whose fundamentals have been assigned in the frequency range 190–430 cm<sup>−1</sup>; (b) CH<sub>3</sub>, CH<sub>2</sub> rocks, and C–C stretches from 750 to 1100 cm<sup>−1</sup>; (c) C–H bends, CH<sub>2</sub> twists, and ring breathing modes from 1100 to 1300 cm<sup>−1</sup>; (d) CH<sub>3</sub> deformations, CH<sub>2</sub> scissors in the frequency interval 1400–1500 cm<sup>−1</sup>, and (e) C–H stretching modes in the highest frequency region of the spectrum from 2900 to 3100 cm<sup>−1</sup>.

A one to one correspondence between the results of the present computation and Durig's classification is only possible for vibrations in the first (a), fourth (d), and fifth (e) regions of the spectrum and not for vibrations in the (b) and (c) regions. For the latter frequencies, a correspondence based on the main contribution to each mode, given in Table II, where we keep the Durig's indexing and labeling scheme for vibrations of *A* (index 1–20) and *B* (index 21–39) symmetry, may in fact be misleading, since, due to the high degeneracy of the vibrational spectrum in this region, each of the harmonic coordinates has several important contributions. Nonetheless, despite considerable differences with respect to Ref. 34 in the expression of the ring modes, we predict similar properties for these vibrations with strongly polarized Raman and low IR activity of the symmetric ring modes ( $\nu_{10}, \nu_{11}$  in Table III) and high IR activity of the asymmetric mode ( $\nu_{34}$  in Table III). It is concluded that any alternative assignment of these two very congested regions of the spectrum must wait until more discriminating vibration-

TABLE I. The computed (a) and the experimental (b) equilibrium geometry of *trans*-(2R-3R)-*trans* dimethylcyclopropane. Values in parentheses have been assumed to interpret electron diffraction data Ref. 31. The definition of the  $\alpha$  and  $\phi$  internal coordinates is given in Fig. 4. The total electronic energy at the equilibrium geometry is computed −195.132 844 hartrees with 6-31G\* orbitals. Bond lengths in angstroms and angles in degrees.

Internal coordinate	(a)	(b)
C <sub>1</sub> –C <sub>2</sub>	1.4999	1.508
C <sub>2</sub> –C <sub>3</sub>	1.4985	1.508
C <sub>2</sub> –C <sub>4</sub>	1.5123	1.519
C <sub>2</sub> –H <sub>4</sub>	1.0787	1.090
C <sub>1</sub> –H <sub>12</sub>	1.0768	1.090
C <sub>4</sub> –H <sub>8</sub>	1.0860	1.089
C <sub>4</sub> –H <sub>9</sub>	1.0863	1.089
C <sub>4</sub> –H <sub>10</sub>	1.0863	1.089
C <sub>2</sub> –C <sub>1</sub> –C <sub>3</sub>	59.9372	(60.0)
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	60.0314	(60.0)
H <sub>4</sub> –C <sub>2</sub> –C <sub>3</sub>	115.3305	
H <sub>4</sub> –C <sub>2</sub> –C <sub>1</sub>	115.5080	
$\alpha$	60.2823	59.9
$\phi$	53.8481	56.8
C <sub>4</sub> –C <sub>2</sub> –C <sub>3</sub>	120.9401	
C <sub>4</sub> –C <sub>2</sub> –C <sub>1</sub>	120.4918	
H <sub>8</sub> –C <sub>4</sub> –C <sub>2</sub>	111.1300	112.1
H <sub>9</sub> –C <sub>4</sub> –C <sub>2</sub>	111.1804	112.1
H <sub>10</sub> –C <sub>4</sub> –C <sub>2</sub>	111.1470	112.1
H <sub>8</sub> –C <sub>4</sub> –H <sub>9</sub>	107.6684	
H <sub>9</sub> –C <sub>4</sub> –H <sub>10</sub>	107.6501	
H <sub>8</sub> –C <sub>4</sub> –H <sub>10</sub>	107.8980	
H <sub>12</sub> –C <sub>1</sub> –H <sub>13</sub>	113.8433	
H <sub>4</sub> –C <sub>2</sub> –C <sub>4</sub> –H <sub>8</sub>	−179.7572	(−180.0)
H <sub>4</sub> –C <sub>2</sub> –C <sub>4</sub> –H <sub>9</sub>	−59.8426	(−60.0)
H <sub>4</sub> –C <sub>2</sub> –C <sub>4</sub> –H <sub>10</sub>	60.3737	(60.0)
H <sub>13</sub> –C <sub>1</sub> –X–C <sub>2</sub>	−89.4288	(−90.0)



TABLE II. Vibrational frequencies and classification for *trans*-(2R-3R) dimethylcyclopropane: 6-31G\* SCF frequencies [column (a)] and experimental *ir* frequencies [column (b)], with Durig's assignment (Ref. 34); IR or Raman data for condensed phases in parenthesis. Nuclear contribution to the vibrational strengths ( $10^{-44}$  cgs units) [column (c)] and total (nuclear plus vibronic contributions [Eq. (31)] rotational strengths [column (d)]. Total rotational strengths computed with 3-21G orbitals in column (e).

Frequency interval	Frequency label	(a)	(b)	(c)	(d)	(e)
190–430 $\text{cm}^{-1}$	$\nu_{20}$	211	194	−1.01	−1.26	−2.22
	$\nu_{39}$	227	208	−3.40	−3.26	−4.55
	$\nu_{19}$	251	293	2.75	1.99	2.21
	$\nu_{38}$	307	230	1.15	−0.38	2.25
	$\nu_{18}$	438	413	6.92	5.24	7.63
	$\nu_{37}$	458	428	−7.86	−2.21	−6.07
750–1100 $\text{cm}^{-1}$	$\nu_{31}$	1074	1070	23.26	14.25	53.72
	$\nu_{32}^?$	1142	(1068)	36.05	27.72	−15.00
	$\nu_{33}$	1210	1019	51.40	32.31	82.39
	$\nu_{34}$	1244	(995)	−40.28	−31.78	−42.52
	$\nu_{35}$	839	970	28.18	30.58	40.57
	$\nu_{14}$	1015	926	24.39	23.19	−56.12
	$\nu_{15}^?$	1298	920	−5.06	−3.60	1.27
	$\nu_{16}$	961	862	−119.05	−97.03	−42.52
	$\nu_{17}$	854	785	−23.57	−22.08	−29.28
	$\nu_{36}$	943	764	−10.67	−7.86	−27.92
	$\nu_{13}$	1261	1097	21.70	16.44	0.05
	$\nu_{30}$	1317	(1100)	3.66	2.99	1.28
1100–1300 $\text{cm}^{-1}$	$\nu_{12}$	1208	1171	50.49	43.78	71.36
	$\nu_{11}$	1592	(1194)	−0.11	−0.08	4.23
	$\nu_{10}$	1349	1219	−1.79	−1.11	10.33
	$\nu_{29}$	1480	1290	61.53	40.38	21.15
	$\nu_{28}$	1569	1384	−13.31	−7.92	−11.57
	$\nu_9$	1554	1411	−38.57	−23.01	−14.37
1400–1500 $\text{cm}^{-1}$	$\nu_8$	1667	(1452)	−6.24	−6.03	−24.19
	$\nu_7$	1638	1459	2.17	1.44	11.24
	$\nu_6$	1644	(1460)	−42.83	−27.44	−31.38
	$\nu_{27}$	1637	1459	−23.18	−14.69	−27.34
	$\nu_{26}$	1645	1473	45.92	25.05	44.97
	$\nu_{25}$	3195	2883	22.03	−27.37	−21.58
2900–3100 $\text{cm}^{-1}$	$\nu_5$	3196	2904	−31.96	30.88	26.57
	$\nu_{24}$	3253	2915	24.30	−31.48	−157.54
	$\nu_4$	3254	2937	−149.81	160.43	172.72
	$\nu_{23}$	3255	2943	−34.76	36.75	173.16
	$\nu_3$	3256	2961	161.43	−162.36	−184.60
	$\nu_2$	3298	3001	77.54	−61.54	−21.85
	$\nu_1$	3308	3010	0.11	−0.09	−23.86
	$\nu_{22}$	3311	3010	−79.92	74.51	57.53
	$\nu_{21}$	3376	3053	7.18	−8.67	−6.98

al properties become available in these frequency ranges.

VCD signs and intensities are likely to provide a more stringent test for the description of the various modes. For vibrations in the (b) and (c) regions large differences are noticed between the absolute values and, in a few instances, even in the signs of the VCD intensities evaluated with the two different sets of atomic orbitals [compare, for instance, the VCD rotational strengths in columns (d) and (e) in Table II]. By a detailed analysis, most of these differences have been traced back to large changes in the vibrational coordinates, proving the high sensitivity of this property to the description of the normal modes. For these reasons, rather than *a priori* prediction of VCD intensities, we consider our results a useful source of information to model the molecular force field against the experimental values of the IR, VCD vibrational frequencies and intensities, when both will

be available for the vibrations in these two spectral regions. A variety of procedures, using reduced sets of empirical scaling factors for the theoretical force field have been recommended also in connection with the interpretation of VCD data.<sup>15,37</sup> In favorable circumstances the use of empirical scaling factors<sup>37</sup> can improve the agreement between calculated and observed fundamentals. However this technique is not so useful when calculating intensities as these are not altered substantially by scaling the force field,<sup>38,39</sup> except where the normal coordinates are very sensitive to the scaling parameters, in which case this approach is clearly inappropriate. In regions (b) and (c) of the spectrum the nature of the vibrational modes is very sensitive to small changes in the force field, and therefore a proper description is not possible without a more detailed force field including anharmonic effects.

TABLE III. Vibrational (km/mol) [column (a)], Raman intensities ( $\text{\AA}^4/\text{amu}$ ) [column (b)], and polarization ratios (Ref. 35) [column (c)] for the ring modes, computed with 6-31G\* orbitals.

Ring mode	Frequency ( $\text{cm}^{-1}$ )	(a)	(b)	(c)
$\nu_{35}$	839	9.11	13.66	0.75
$\nu_{14}$	1015	1.16	9.91	0.32
$\nu_{10}$	1349	0.52	14.83	0.17

### C–H IR, VCD frequencies and intensities

For all remaining regions of the spectrum (a), (d), and (e), our results do not suffer from the above limitations. A consistent description of the vibrational coordinates, of their labeling and of the VCD signs has been obtained with the two orbital bases. This is especially true for the C–H vibrations, for which the expressions of the normal modes are essentially determined, as discussed in detail in the following section, by symmetry constraints: the local pseudo- $C_{3v}$  symmetry of the methyl groups and the overall  $C_2$  molecular symmetry. For these coordinates, in addition to the VCD intensities quoted in Table II, we report in Table IV, the computed IR intensities. The two sets of values given in Table IV, although differing in the absolute values, reflect qualitatively the intensity distribution in the two spectra of Figs. 2 and 3, once the degeneracy of the various modes is taken into account.

### V. DISCUSSION

The theoretical frequencies and intensities relevant for the interpretation of the available spectral data, which are confined to the C–H stretching region of the spectrum, are collected in Tables II and IV.

According to these results, the IR band with center at  $2880\text{ cm}^{-1}$ , assigned to the two methyl C–H symmetric stretching modes ( $\nu_{25}, \nu_5$ ) splits into two VCD bands of opposite signs. The actual form of the VCD absorption is related to the frequency ordering of the two vibrations. The disappearance of the IR band in the gas phase VCD spectrum would indicate almost perfect degeneracy of the two components and opposite rotational strengths in agreement with the results of our computation. On the other hand, the two components split in  $\text{CCl}_4$  solution, where they generate a nearly conservative VCD couplet. Our computed VCD intensities suggest the frequency order  $\nu_{25} < \nu_5$  in this medium, in agreement with the order of VCD signs in Fig. 3.

The next IR band centered at  $2960\text{ cm}^{-1}$  in the vapor spectrum is highly structured suggesting a superposition of several vibrational transitions. This is apparent in the solution spectrum where four vibrational peaks are clearly seen. It is even more apparent in the gas phase VCD spectrum, where the band splits into a rather spectacular sequence of four narrow, very intense bands with alternate VCD signs. The experimental spectrum and the computed VCD intensities suggest the frequency ordering  $\nu_{24} < \nu_4 < \nu_3 < \nu_{23}$ .

These first two C–H bands of the VCD spectrum pro-

TABLE IV. Infrared intensities (Refs. 14 and 35) (km/mol) computed for the CH stretching modes with 3-21G [column (a)] and 6-31G\* [column (b)] orbitals.

Frequency label	Description	(a)	(b)
$\nu_{25}$	$\text{CH}_3$ symmetric	61.55	89.00
$\nu_5$	$\text{CH}_3$ symmetric	8.08	10.59
$\nu_{24}$	$\text{CH}_3$ antisymmetric	13.33	7.32
$\nu_4$	$\text{CH}_3$ antisymmetric	49.71	70.75
$\nu_{23}$	$\text{CH}_3$ antisymmetric	44.79	66.71
$\nu_3$	$\text{CH}_3$ antisymmetric	9.79	11.03
$\nu_2$	$\text{CH}_2$ symmetric	17.28	32.85
$\nu_1$	CH symmetric	1.03	0.00
$\nu_{22}$	CH antisymmetric	27.67	61.45
$\nu_{21}$	$\text{CH}_2$ antisymmetric	15.03	28.67

vide two interesting cases of degenerate vibrations and their VCD intensities are easily explained using group theoretical arguments and slight modifications and extension of perturbation theory for VCD of degenerate vibrations.<sup>36</sup>

According to this theory, perfect  $C_{3v}$  local symmetry of the two methyl groups is assumed in the chiral molecule to write the lowest excited vibrational states for the methyl symmetric C–H stretching modes as

$$\begin{aligned}\frac{1}{\sqrt{2}} \{[10] + [01]\} &= \frac{1}{\sqrt{2}} [a + b], \\ \frac{1}{\sqrt{2}} \{[10] - [01]\} &= \frac{1}{\sqrt{2}} [a - b].\end{aligned}\quad (35)$$

Here,  $a$  and  $b$  denote vibrational excitations localized on either one of the two methyl groups. This assumption appears to be justified in our case given the computed methyl equilibrium geometry and the actual expression for the relevant modes. We then obtain the rotational strengths

$$\begin{aligned}\frac{1}{2}\Im(d_a \cdot m_a + d_b \cdot m_b + d_a \cdot m_b + d_b \cdot m_a), \\ \frac{1}{2}\Im(d_a \cdot m_a + d_b \cdot m_b - d_a \cdot m_b - d_b \cdot m_a).\end{aligned}\quad (36)$$

The first two terms vanish due to the local  $C_{3v}$  symmetry of the two methyl groups. The remaining two terms sum to zero in an achiral molecular as in the corresponding meso (*cis*) form

$$d_a \cdot m_b = -d_b \cdot m_a. \quad (37)$$

If we assume that the only effect of the chiral structure is to remove the equality (37), two opposite rotational strengths are obtained for the two vibrational transitions. Our computed rotational strengths agree with this description and provide an estimate for the coupling term ( $d_a \cdot m_b + d_b \cdot m_a$ ).

Similarly we write the symmetrized molecular vibrational states for the four methyl asymmetric stretching modes

$$\begin{aligned}
& \frac{1}{2}\{[1000] + [0100] + [0010] + [0001]\} \\
&= \frac{1}{2}[a + a' + b + b'], \\
& \frac{1}{2}\{[1000] - [0100] + [0010] - [0001]\} \\
&= \frac{1}{2}[a - a' + b - b'], \\
& \frac{1}{2}\{[1000] + [0100] - [0010] - [0001]\} \\
&= \frac{1}{2}[a + a' - b - b'], \\
& \frac{1}{2}\{[1000] + [0100] - [0010] - [0001]\} \\
&= \frac{1}{2}[a + a' - b - b'], \\
& \frac{1}{2}\{[1000] - [0100] - [0010] + [0001]\} \\
&= \frac{1}{2}[a - a' - b + b'],
\end{aligned} \tag{38}$$

where  $(a, a')$ ,  $(b, b')$  are two degenerate vibrational excitation localized on either one of the two methyl groups now interacting through the molecular chiral environment. Using the same type of arguments, the following vibrational strengths are derived

$$\begin{aligned}
& \frac{1}{2}\Re(+d_a \cdot m_{a'} + d_{a'} \cdot m_a + d_a \cdot m_{b'} + d_{b'} \cdot m_a), \\
& \frac{1}{2}\Re(-d_a \cdot m_{a'} - d_{a'} \cdot m_a - d_a \cdot m_{b'} - d_{b'} \cdot m_a), \\
& \frac{1}{2}\Re(+d_a \cdot m_{a'} + d_{a'} \cdot m_a - d_a \cdot m_{b'} - d_{b'} \cdot m_a), \\
& \frac{1}{2}\Re(-d_a \cdot m_{a'} - d_{a'} \cdot m_a + d_a \cdot m_{b'} + d_{b'} \cdot m_a),
\end{aligned} \tag{39}$$

where we have intragroup coupling terms  $(d_a \cdot m_{a'}, d_{a'} \cdot m_a)$  in addition to intergroup coupling as in the previous example. According to Eq. (39), for each symmetry two vibrations are predicted with opposite rotational strengths as indeed found in our computations. The difference between the absolute values of the VCD intensities of the two pairs should reflect the importance of the intergroup coupling terms. Apparently, these terms are quite sensitive to subtle changes in the description of the molecular electronic structure. With the reduced set of orbitals, we evaluate nearly equal absolute intensities for all four stretching modes suggesting very small intergroup coupling terms. With the extended set of orbitals, the two pairs of values differ considerably and are indicative of large intergroup coupling terms.

The IR band at  $3010 \text{ cm}^{-1}$  is assigned to the C-H  $\nu_{22}$  and  $\nu_1$  and to the symmetric  $\text{CH}_2$  stretching mode  $\nu_2$ ; the antisymmetric  $\text{CH}_2$  stretching vibration  $\nu_{21}$  is assigned to the IR band at  $3060 \text{ cm}^{-1}$ . The VCD intensity of  $\nu_1$  is estimated to be almost zero but the rotational strengths computed for  $\nu_2$  and  $\nu_{22}$  are consistent with the profile of the VCD spectrum in this frequency region.

For the two CH vibrations  $\nu_1$  and  $\nu_{22}$  degenerate perturbation theory no longer holds, since these two vibrations are intrinsically chiral, and, as a consequence, the local contribution to chirality [ $d_a \cdot m_a$  terms in Eq. (36)] cannot be disregarded. Nonetheless, from the coupling of the two C-H vibrations we expect one optically active and one optically inactive vibration as indeed found in the actual computation (see Table II). Similarly the chirality of the  $\text{CH}_2$  vibrations is related to the chiral equilibrium structure of the group (see Table I).

The rotational strength of the asymmetric  $\text{CH}_2$  stretching mode is predicted to be negative. The rotational envelope gives to the band a fairly complex structure, with apparent

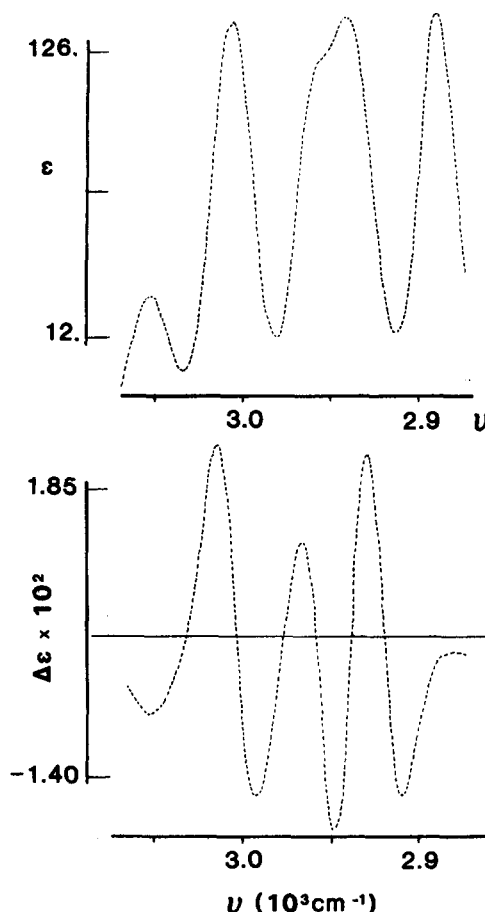


FIG. 5. Simulated IR (upper) and VCD (lower) spectra (see the text) for the CH stretching region. Extinction coefficients  $\epsilon$  and circular dichroism  $\Delta\epsilon = \epsilon^- - \epsilon^+$  in the frequency range  $2850\text{--}3050 \text{ cm}^{-1}$ .

suppression of the VCD absorption in the  $Q$  branch.

Simulations of the IR and VCD spectra are presented in Fig. 5. These were obtained using the experimental frequencies for all CH modes [column (b) in Table II] apart from the two symmetric  $\text{CH}_3$  stretches ( $\nu_{25}, \nu_5$ ) which, in agreement with the proposed assignment, were taken to be degenerate at  $2889 \text{ cm}^{-1}$ . Calculated IR and VCD intensities were used (6-31G\* orbitals). The band shape expressions were taken from Refs. 40 and 41 and the bandwidth reduced to  $\sqrt{\nu_i/5}$  for all CH vibrations. The overall shapes of these simulated IR and VCD spectra reproduce the experimental IR and VCD absorptions in Fig. 2 extremely well, giving support to our assignment.

An important conclusion we draw from these results concerns the relative importance of the electronic and the nuclear components of the rotational strengths. As seen from the comparison of values in columns (c) and (d) in Table II, the two contributions always have opposite signs. The electronic term has lower absolute value than the nuclear term for all lower frequency modes and, therefore, does not determine the sign of the corresponding VCD bands. It becomes the dominant factor and determines the VCD signs and intensities for all C-H stretching vibrations.

For vibrations in the first class, our results do not con-

flict with the commonly accepted picture of VCD as arising from vibrations of partially screened nuclear charges.<sup>42,43</sup> For vibrations in the second class, this picture is changed since the dominant term is now the electronic term, requiring the explicit inclusion of the ground electronic molecular wave function.

The great importance of vibronic effects for VCD of C–H vibrations bear some resemblance with the theory of radiationless decay of aromatic hydrocarbons where C–H vibrations play a very special role as acceptor modes.<sup>44–46</sup> This resemblance is even more apparent in the approximate Eq. (34), showing the inverse relationship with the electronic excitation energy. In this connection, they act as promoting modes to induce differential vibronic interactions for the ground and excited vibrational states.

## VI. CONCLUSIONS

A computation has been presented of VCD intensities for *trans*-dimethylcyclopropane from SCF molecular wave functions and with the inclusion of the vibronic contributions to VCD according to Stephens theory<sup>5</sup> and Amos<sup>15</sup> implementation within the CADPAC<sup>14</sup> program. The results confirm the importance of the electronic terms, and indicate that these are the dominant terms determining the VCD signs and intensities of all C–H stretching vibrations. The results for these vibrations are found in agreement with the available experimental information and are easily rationalized using group theoretical arguments. The results indicate that the VCD signs and intensities are very sensitive probes of the expressions of the normal modes and, therefore, the VCD intensities computed for all remaining frequencies provide a basis for the assignment of the normal modes in the congested regions of the spectrum, when new VCD data will become available for the molecule, in these frequency ranges.

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