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***Ab initio* calculations of anharmonic vibrational circular dichroism intensities of *trans*-2,3-dideuteriooxirane**

Keld L. Bak,^{a)} Ota Bludský,^{b)} and Poul Jørgensen

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

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A priori theory is derived for anharmonic calculations of vibrational circular dichroism (VCD). The anharmonic VCD expression is gauge origin independent and reduce to the magnetic field perturbation theory expression in the double-harmonic approximation. The theory has been implemented using second-order contact transformations for the vibration problem. Zeroth, first, and diagonal second derivatives of the atomic axial tensor are needed at the molecular equilibrium geometry. *Ab initio* calculations have been carried out for *trans*-2,3-dideuteriooxirane using self consistent field theory for the atomic axial tensors and using second-order Møller–Plesset theory for the atomic polar tensors and the force fields. The changes of the vibrational rotatory strengths from anharmonicities are small, and do not explain the previously observed large discrepancies between the double-harmonic results and the experimental values for three out of the 15 vibrational modes. © 1995 American Institute of Physics.

I. INTRODUCTION

The electronic part of the magnetic dipole transition moment vanishes for vibrational transitions within the Born–Oppenheimer (BO) approximation. It must therefore be treated beyond the BO approximation in proper expressions for vibrational circular dichroism (VCD). The first attempt in developing a theory beyond the BO was presented by Craig and Thirunamachandran.¹ More satisfactory derivations have been presented by Nafie and Freedman² and Stephens.³ The vibronic coupling theory of Nafie and Freedman² use perturbation theory to describe through first order in the non-BO couplings the vibrational magnetic dipole transition moments. The theory of Stephens¹ is in line with the vibronic coupling theory and the non-BO effects are treated at the same level of perturbation theory. Stephens identifies in the transition elements the response of an electronic wave function to a magnetic field and exploits this to rewrite the non-BO magnetic dipole transition moments to involve only the electronic reference state. Transforming these equations to normal coordinates Stephens gives an *a priori* VCD theory which is well suited for implementations in *ab initio* computer programs. The theory of Stephens is known as magnetic field perturbation theory.

Both the vibronic coupling theory and the magnetic field perturbation theory have been used. For small and medium sized rigid molecules *ab initio* VCD spectra calculated within the double-harmonic approximation from these theories generally agree reasonably well with experiment.^{4–26} Most calculations are carried out at the Hartree–Fock level but more recently correlated calculations have been presented enhancing the accuracy of the calculated spectra.^{11,16,22–27}

The *trans*-2,3-dideuteriooxirane molecule has become a

benchmark system for such calculations since the size of the molecule allows relatively extensive basis sets to be used.^{17–26} Calculations have been carried out using the Hartree–Fock, MP2 (second-order Møller–Plesset perturbation theory), MCSCF (multiconfigurational SCF), and DFT (density functional theory) theories. For most transitions the Hartree–Fock VCD-spectrum agrees reasonably with experiment²⁸ and the agreement is enhanced when correlation is included in the calculation. At the MP2 level the only major discrepancies with experiment are for the two C–H stretchings (mode 1 and 2) and the mode at 1235 cm^{−1}.²² It has been suggested that anharmonicity, which is not included in these calculations, might be responsible for the discrepancies. The previously derived *a priori* VCD theories (the vibronic coupling theory and the magnetic field perturbation theory) are based on the Condon approximation and can not be used to describe anharmonic effects.

In this work we present a more general VCD theory which go beyond the Condon approximation and therefore can be used to describe anharmonic effects. As in the previous theories the electronic part of the magnetic dipole transition moment is treated to first order in the non-BO couplings and in the limit of the double harmonic approximation the derived vibrational rotatory strength reduce to the magnetic field perturbation theory expression.

The anharmonic effects are calculated for *trans*-2,3-dideuteriooxirane. The anharmonicities are included using perturbation theory based on contact transformations.^{29,31} Contact transformation theory has previously been successfully applied in anharmonic *ab initio* calculations of vibrational frequencies and absorption intensities for a few sizable molecules including *trans*-2,3-dideuteriooxirane.^{32–36}

II. ANHARMONIC VIBRATIONAL CIRCULAR DICHROISM THEORY

In the vibronic coupling theory the Herzberg–Teller couplings and the non-BO couplings are treated to first order.² Magnetic dipole transition elements, which are first order in

^{a)}Permanent address: UNI-C, Olof Palmes Allé 38, DK-8200 Aarhus N, Denmark.

^{b)}Permanent address: J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic.

the non-BO couplings, are therefore only treated to zeroth order in the Herzberg–Teller coupling. This is the equivalent to using the Condon approximation to derive the magnetic field perturbation theory expressions.³ The vibronic coupling theory and the magnetic field perturbation theory therefore cannot straightforwardly be used to obtain anharmonic effects.

In this section we derive an *a priori* VCD theory to describe anharmonic effects. The theory is not limited to the Condon approximation or to the assumption of harmonicity. The same fundamental assumptions are used as in the vibronic coupling theory² and the magnetic field perturbation theory.³ The non-BO couplings are treated to first order in perturbation theory and the derived expression reduce in the limit of the double-harmonic approximation to the magnetic field perturbation theory expressions. We also prove that the theory gives gauge origin independent VCD results.

A. The vibrational rotatory strength

The intensities in VCD are determined by the vibrational rotatory strength. For the a th mode corresponding to a vibrational transition $Om \rightarrow On$ the rotatory strength is

$$R_a \equiv R(Om \rightarrow On) = \text{Im}[\langle Om | \boldsymbol{\mu} | On \rangle \langle On | \mathbf{m} | Om \rangle], \quad (1)$$

where $\boldsymbol{\mu} = \boldsymbol{\mu}^e + \boldsymbol{\mu}^n$ and $\mathbf{m} = \mathbf{m}^e + \mathbf{m}^n$ are the electronic and magnetic dipole operators both consisting of an electronic and a nuclear part

$$\boldsymbol{\mu}^e = - \sum_i \mathbf{r}_i, \quad \boldsymbol{\mu}^n = \sum_{\lambda} Z_{\lambda} \mathbf{R}_{\lambda}, \quad (2)$$

$$\mathbf{m}^e = - \frac{1}{2} \sum_i \mathbf{r}_i \times \mathbf{p}_i, \quad \mathbf{m}^n = \sum_{\lambda} \left(\frac{Z_{\lambda}}{2M_{\lambda}} \right) \mathbf{R}_{\lambda} \times \mathbf{P}_{\lambda}. \quad (3)$$

Here \mathbf{r}_i and \mathbf{p}_i are the position and momentum of the i th electron and Z_{λ} , M_{λ} , \mathbf{R}_{λ} , and \mathbf{P}_{λ} are the charge, mass, position, and momentum of the λ th nucleus. The formulas are expressed in atomic units and are derived from the SI unit formulas. The states Om and On can be viewed as exact or approximate states depending on the level of theory. In this work Born–Oppenheimer wave functions are used to obtain the electric dipole moments and the nuclear part of the magnetic dipole moment. To describe the electronic part of the magnetic dipole moment Born–Oppenheimer states have been corrected to first order in non-BO couplings.

To show how the non-BO corrections are introduced the next subsection is used to shortly present the Born–Oppenheimer approximation and the perturbation theory needed. Thereafter the individual transition moments and the rotatory strength are evaluated and analyzed.

B. The Born–Oppenheimer approximation and perturbation corrections

For a molecular system the nonrelativistic Hamiltonian is a sum of the electronic Hamiltonian, H_E , and the nuclear kinetic energy operator, T_N

$$H = H_E + T_N. \quad (4)$$

The electronic eigenfunctions $\varphi_P(\mathbf{r}; \mathbf{R})$ of the electronic Hamiltonian are functions of the electronic coordinates \mathbf{r} , and depends parametrically on the nuclear coordinates \mathbf{R} . Since these eigenfunctions span the electronic space, the eigenfunctions of H can be expanded in these functions as

$$\Psi_P(\mathbf{r}, \mathbf{R}) = \sum_P \varphi_P(\mathbf{r}; \mathbf{R}) \tilde{\chi}_{Pp}(\mathbf{R}). \quad (5)$$

Taking this form of the exact wave functions T_N can be divided into a sum of two operators T_{N1} and T_{N2} which are defined by their operations on the wave functions

$$T_{N1} \varphi_P \tilde{\chi}_{Pp} = \varphi_P (T_N \tilde{\chi}_{Pp}), \quad (6)$$

$$T_{N2} \varphi_P \tilde{\chi}_{Pp} = (T_N \varphi_P) \tilde{\chi}_{Pp} - \sum_{\lambda \alpha} \frac{1}{M_{\lambda}} \left(\frac{\partial \varphi_P}{\partial R_{\lambda \alpha}} \right) \left(\frac{\partial \tilde{\chi}_{Pp}}{\partial R_{\lambda \alpha}} \right), \quad (7)$$

where $R_{\lambda \alpha}$ denotes the α Cartesian component of \mathbf{R}_{λ} . The Hamiltonian can then be written as

$$H = H_{BO} + T_{N2}, \quad (8)$$

where the Born–Oppenheimer Hamiltonian is defined as

$$H_{BO} \equiv H_E + T_{N1}. \quad (9)$$

In the Born–Oppenheimer approximation H is approximated by H_{BO} . The eigenfunctions of the Born–Oppenheimer Hamiltonian are simple products of electronic eigenfunctions and vibrational wave functions

$$H_{BO} \varphi_P \chi_{Pp} = \varphi_P (E_P + T_N) \chi_{Pp} = \varphi_P \chi_{Pp} E_{Pp}. \quad (10)$$

Here $E_P(\mathbf{R})$ is the electronic energy corresponding to $\varphi_P(\mathbf{r}; \mathbf{R})$ and E_{Pp} is the Born–Oppenheimer vibronic energy corresponding to the BO vibronic wave function $\varphi_P(\mathbf{r}; \mathbf{R}) \chi_{Pp}(\mathbf{R})$. Notice that the vibrational wave functions $\chi_{Pp}(\mathbf{R})$ are different from the nuclear wave functions $\tilde{\chi}_{Pp}(\mathbf{R})$ in Eq. (5).

The approximations made in Born–Oppenheimer theory can be corrected by perturbation theory using the vibronic coupling operator T_{N2} as the perturbation operator. For a nondegenerate Born–Oppenheimer wave function $\varphi_O \chi_{On}$ the wave function corrected to first order for non-BO vibrational couplings becomes

$$\Psi_{On} = \varphi_O \chi_{On} + \sum_{P \neq O, p} \varphi_P \chi_{Pp} a_{Pp, On}, \quad (11)$$

where the expansion coefficients are given as

$$a_{Pp, On} = \frac{\langle \varphi_P \chi_{Pp} | T_{N2} | \varphi_O \chi_{On} \rangle}{E_{On} - E_{Pp}}. \quad (12)$$

The perturbation theory only restricts the summation in Eq. (11) to $Pp \neq On$ but it is easily seen that $a_{Pp, On} = 0$ for $P = O$ and the summation can therefore be restricted as in Eq. (11).

C. The electric dipole moment for vibrational transitions

The Born–Oppenheimer approximation is used for evaluating both the electronic and the nuclear part of the electric dipole transition moments for the vibrational transi-

tion $On \rightarrow Om$. Both elements are nonvanishing and easily evaluated from Eq. (2). The electronic and the nuclear part of the electric dipole transition moment are

$$\mu_{On,Om}^e = \langle \chi_{On} | \langle \varphi_O | - \sum_i \mathbf{r}_i | \varphi_O \rangle | \chi_{Om} \rangle, \quad (13)$$

$$\mu_{On,Om}^n = \langle \chi_{On} | \sum_{\lambda} Z_{\lambda} \mathbf{R}_{\lambda} | \chi_{Om} \rangle, \quad (14)$$

and the total electric dipole transition moment which results from adding these two terms is

$$\mu_{On,Om} = \langle \chi_{On} | \mu_{OO} | \chi_{Om} \rangle, \quad (15)$$

where the operator $\mu_{OO}(\mathbf{R})$ is defined as

$$\mu_{OO} = \langle \varphi_O | - \sum_i \mathbf{r}_i | \varphi_O \rangle + \sum_{\lambda} Z_{\lambda} \mathbf{R}_{\lambda}. \quad (16)$$

D. The magnetic dipole moment for vibrational transitions

The nuclear contribution to the magnetic dipole transition moment is also evaluated within the BO approximation. Using Eq. (3), for the vibrational transition $On \rightarrow Om$ it becomes

$$\mathbf{m}_{On,Om}^n = \sum_{\lambda} \frac{Z_{\lambda}}{2M_{\lambda}} \langle \chi_{On} | \mathbf{R}_{\lambda} \times \mathbf{P}_{\lambda} | \chi_{Om} \rangle \quad (17a)$$

$$= \sum_{\lambda\alpha} \frac{-2}{M_{\lambda}} \langle \chi_{On} | \mathbf{J}_{\alpha}^{\lambda} \frac{\partial}{\partial R_{\lambda\alpha}} | \chi_{Om} \rangle, \quad (17b)$$

where the nuclear part of the atomic axial tensor (AAT) $\mathbf{J}_{\alpha}^{\lambda}(\mathbf{R})$ is defined as

$$\mathbf{J}_{\alpha}^{\lambda} = \frac{i}{4} \sum_{\beta\gamma} \varepsilon_{\alpha\beta\gamma} Z_{\lambda} R_{\lambda\gamma} \mathbf{e}_{\beta}. \quad (18)$$

Here $\varepsilon_{\alpha\beta\gamma}$ is the antisymmetric unit third rank tensor and \mathbf{e}_{β} is a unit vector along the β th Cartesian coordinate.

As easily verified the electronic part of the magnetic dipole transition moment vanishes within the Born–Oppenheimer approximation for the vibrational transition $On \rightarrow Om$. This is an artefact of uncoupling the electronic and nuclear motions. The electronic part of the magnetic dipole transition moment therefore must be treated beyond the BO approximation. To first order in the vibronic coupling it becomes

$$\mathbf{m}_{On,Om}^e \equiv \langle \Psi_{On} | \mathbf{m}^e | \Psi_{Om} \rangle = \mathbf{B}_{On,Om} - \mathbf{B}_{Om,On}, \quad (19)$$

where

$$\mathbf{B}_{On,Om} \equiv \sum_{P \neq O, p} \langle \varphi_O \chi_{On} | \mathbf{m}^e | \varphi_P \chi_{Pp} \rangle a_{Pp,Om}. \quad (20)$$

In Eq. (19) the electronic and the vibrational wave functions are assumed to be real and we have used that \mathbf{m}^e is Hermitian and purely imaginary. The denominator in $a_{Pp,On}$ can be rewritten as

$$\frac{1}{E_{On} - E_{Pp}} = \frac{1}{E_O(\mathbf{R}) - E_P(\mathbf{R})} - \frac{(E_{On} - E_{Pp}) - (E_O(\mathbf{R}) - E_P(\mathbf{R}))}{(E_O(\mathbf{R}) - E_P(\mathbf{R}))(E_{On} - E_{Pp})}. \quad (21)$$

$(E_{On} - E_{Pp}) - (E_O(\mathbf{R}) - E_P(\mathbf{R}))$ is essentially the difference in vibrational energy for $Pp \rightarrow On$. If this difference is small compared to the difference in vibronic energy then $[(E_{On} - E_{Pp}) - (E_O(\mathbf{R}) - E_P(\mathbf{R}))]/(E_{On} - E_{Pp}) \ll 1$ and the denominator in $a_{Pp,On}$ can be approximated by

$$\frac{1}{E_{On} - E_{Pp}} \cong \frac{1}{E_O(\mathbf{R}) - E_P(\mathbf{R})}. \quad (22)$$

Equation (22) is not generally valid, but if φ_O is the electronic ground state wave function and χ_{On} is a low-lying vibrational state the equation is usually fulfilled. Concentrating on fundamental vibrational transitions on the electronic ground state it is thus justified to use Eq. (22). The coefficients $a_{Pp,Om}$ may be further simplified by using the identity $\sum_p |\chi_{Pp}\rangle \langle \chi_{Pp}| = 1$ and Eq. (20) becomes

$$\mathbf{B}_{On,Om} = \sum_{P \neq O} \langle \chi_{On} | \frac{\langle \varphi_O | \mathbf{m}^e | \varphi_P \rangle \langle \varphi_P | T_{N2} | \varphi_O \rangle}{E_O - E_P} | \chi_{Om} \rangle. \quad (23)$$

The electronic interaction of a molecular system with a uniform magnetic flux density, \mathbf{B} , is to first order in \mathbf{B} represented by the interaction operator $-\mathbf{m}^e \mathbf{B}$ and the linear response of the electronic wave function to the magnetic flux density becomes

$$\frac{\partial |\varphi_O\rangle}{\partial \mathbf{B}} = - \sum_{P \neq O} |\varphi_P\rangle \frac{\langle \varphi_P | \mathbf{m}^e | \varphi_O \rangle}{E_O - E_P}. \quad (24)$$

Equation (23) can hence be re-expressed as

$$\mathbf{B}_{On,Om} = - \langle \chi_{On} | \left\langle \frac{\partial \varphi_O}{\partial \mathbf{B}} \right| T_{N2} | \varphi_O \rangle | \chi_{Om} \rangle. \quad (25)$$

The electronic part of the magnetic dipole transition moment is obtained by inserting Eq. (25) in (19) and using the operator T_{N2} as defined in Eq. (7). Since the contributions from the first term in Eq. (7) vanish it gives

$$\mathbf{m}_{On,Om}^e = \sum_{\lambda\alpha} \frac{1}{M_{\lambda}} \left(\langle \chi_{Om} | \mathbf{I}_{\alpha}^{\lambda} \frac{\partial}{\partial R_{\lambda\alpha}} | \chi_{On} \rangle - \langle \chi_{On} | \mathbf{I}_{\alpha}^{\lambda} \frac{\partial}{\partial R_{\lambda\alpha}} | \chi_{Om} \rangle \right), \quad (26)$$

where the electronic part of the atomic axial tensor (AAT) $\mathbf{I}_{\alpha}^{\lambda}(\mathbf{R})$ is defined as

$$\mathbf{I}_{\alpha}^{\lambda} \equiv \left\langle \frac{\partial \varphi_O}{\partial R_{\lambda\alpha}} \right| \frac{\partial \varphi_O}{\partial \mathbf{B}} \rangle. \quad (27)$$

The total magnetic dipole transition moment for the vibrational transition $On \rightarrow Om$ which results from adding $\mathbf{m}_{On,Om}^e$ and $\mathbf{m}_{On,Om}^n$ is

$$\mathbf{m}_{On,Om} = \langle \chi_{Om} | \mathbf{m}_{OO} | \chi_{On} \rangle - \langle \chi_{On} | \mathbf{m}_{OO} | \chi_{Om} \rangle, \quad (28)$$

where the operator $\mathbf{m}_{OO}(\mathbf{R})$ is defined as

$$\mathbf{m}_{OO} = \sum_{\lambda\alpha} \frac{1}{M_\lambda} (\mathbf{I}_\alpha^\lambda + \mathbf{J}_\alpha^\lambda) \frac{\partial}{\partial R_{\lambda\alpha}}. \quad (29)$$

E. Gauge origin dependence of the vibrational rotatory strength

The rotatory strengths for fundamental vibrations are obtained inserting the electric and magnetic dipole transition moments, Eqs. (15) and (28), in Eq. (1). Rotatory strengths are physical observable and must be independent of the gauge origin of the external magnetic vector potential. In the following we show that the obtained vibrational rotatory strength is gauge origin independent.

Consider changing the gauge origin for the external magnetic vector potential, \mathbf{A} , from \mathbf{O}_1 to $\mathbf{O}_2 = \mathbf{O}_1 + \mathbf{V}$ where \mathbf{V} is a constant vector. The electric dipole operators and therefore the electric dipole transition moments are not affected by this change. In contrast the electronic and the nuclear part of the magnetic dipole operator changes as the electronic and nuclear coordinates in this operator refer to the gauge origin. The magnetic dipole operators at the new gauge origin are

$$\mathbf{m}^{e(O_2)} = \mathbf{m}^{e(O_1)} + \frac{1}{2} \mathbf{V} \times \sum_i \mathbf{p}_i, \quad (30)$$

$$\mathbf{m}^{n(O_2)} = \mathbf{m}^{n(O_1)} - \mathbf{V} \times \sum_\lambda \left(\frac{Z_\lambda}{2M_\lambda} \right) \mathbf{P}_\lambda. \quad (31)$$

The electronic part of the atomic axial tensor at the new gauge origin is found from Eq. (30) by inserting Eq. (24) in Eq. (27)

$$\mathbf{I}_\alpha^{\lambda(O_2)} = \mathbf{I}_\alpha^{\lambda(O_1)} - \frac{i}{4} \mathbf{V} \times \frac{\partial \boldsymbol{\mu}_{OO}^e}{\partial R_{\lambda\alpha}}. \quad (32)$$

To derive this equality we have employed the off-diagonal hypervirial relation

$$\langle \varphi_P | \mathbf{p}_i | \varphi_0 \rangle = -i(E_0 - E_P) \langle \varphi_P | \mathbf{r}_i | \varphi_0 \rangle. \quad (33)$$

The gauge origin dependence of the electronic part of the magnetic dipole transition moment is determined inserting Eq. (32) in Eq. (26). The resulting expression is simplified by integrating each of the two matrix elements by parts and utilizing that the vibrational states, χ_{On} and χ_{Om} , are eigenfunctions of the vibrational Hamiltonian, $E_O + T_N$. The simplified expression is

$$\mathbf{m}_{On,Om}^{e(O_2)} = \mathbf{m}_{On,Om}^{e(O_1)} - \frac{i}{2} \omega_{nm} \mathbf{V} \times \boldsymbol{\mu}_{On,Om}^e, \quad (34)$$

where the vibrational excitation energy is defined as

$$\omega_{nm} \equiv (E_{On} - E_{Om}). \quad (35)$$

The nuclear part of the magnetic dipole transition moment at the new gauge origin is easily evaluated inserting Eq. (31) in Eq. (17)

$$\mathbf{m}_{On,Om}^{n(O_2)} = \mathbf{m}_{On,Om}^{n(O_1)} - \frac{i}{2} \omega_{nm} \mathbf{V} \times \boldsymbol{\mu}_{On,Om}^n. \quad (36)$$

Here we have used the off-diagonal hypervirial relation for vibrational states

$$\langle \chi_{On} | \mathbf{P}_\lambda | \chi_{Om} \rangle = -iM_\lambda \omega_{mn} \langle \chi_{On} | \mathbf{R}_\lambda | \chi_{Om} \rangle. \quad (37)$$

Adding Eqs. (34) and (36) the gauge origin dependence of the total magnetic dipole transition moment is obtained

$$\mathbf{m}_{On,Om}^{(O_2)} = \mathbf{m}_{On,Om}^{(O_1)} - \frac{i}{2} \omega_{nm} \mathbf{V} \times \boldsymbol{\mu}_{On,Om}. \quad (38)$$

Utilizing this equation to evaluate the vibrational rotatory strength at the new gauge origin, it is seen that the rotatory strength is gauge origin independent

$$R_i^{(O_2)} = \text{Im}(\boldsymbol{\mu}_{On,Om} \cdot \mathbf{m}_{On,Om}^{(O_2)}) = R_i^{(O_1)}. \quad (39)$$

F. The double-harmonic approximation

In the double-harmonic approximation the electric dipole transition moment Eq. (15) reduce to the expression that is conventionally used in *ab initio* VCD calculations.³ We will now show that the magnetic dipole transition moment Eq. (28) also simplifies to the expression that normally is used in *ab initio* VCD calculations. Using the Condon approximation in Eq. (29) [i.e., $\mathbf{I}_\alpha^\lambda(\mathbf{R})$ and $\mathbf{J}_\alpha^\lambda(\mathbf{R})$ are approximated by their equilibrium geometry values $\mathbf{I}_\alpha^{\lambda 0}$ and $\mathbf{J}_\alpha^{\lambda 0}$] the magnetic dipole transition moment Eq. (28) becomes

$$\mathbf{m}_{On,Om} = - \sum_{\lambda\alpha} \frac{2}{M_\lambda} (\mathbf{I}_\alpha^{\lambda 0} + \mathbf{J}_\alpha^{\lambda 0}) \langle \chi_{On} | \frac{\partial}{\partial R_{\lambda\alpha}} | \chi_{Om} \rangle. \quad (40)$$

When the harmonic approximation is applied for the electronic potential we obtain

$$\mathbf{m}_{Og,Oe}^{\text{DH}} = -\sqrt{2\omega_a} \sum_{\lambda\alpha} (\mathbf{I}_\alpha^{\lambda 0} + \mathbf{J}_\alpha^{\lambda 0}) S_{\alpha,a}^\lambda, \quad (41)$$

where $S_{\alpha,a}^\lambda$ is the Cartesian to normal coordinate transformation matrix and a labels the normal mode for the fundamental transition $Og \rightarrow Oe$ with the excitation energy ω_a . The superscript DH is used to denote that Eq. (41) represents the magnetic dipole transition moment in the double-harmonic approximation. Equation (41) is the expression that is used in magnetic field perturbation theory.³

III. CONTACT TRANSFORMATION THEORY FOR ANHARMONIC MAGNETIC DIPOLE TRANSITION MOMENTS

Contact transformation theory has been widely used to treat molecular rotation–vibration problems.^{29–31} Recently it has also proven to be useful for *ab initio* evaluation of vibrational properties where especially the evaluation of anharmonic corrections to vibrational frequencies and electric dipole moments has been considered.^{32–36} In this section we extend the treatment to the magnetic dipole transition moments in Eq. (28).

We use the dimensionless normal coordinates q_a , related to the normal coordinates Q_a as $q_a = \sqrt{\omega_a} Q_a$, and the conjugated momentum operators $p_a = -i(\partial/\partial q_a)$. In these coordinates the operator in Eq. (29) becomes

$$\mathbf{m}_{OO} = \sum_a A^a(\mathbf{q}) p_a, \quad (42)$$

where the coefficients

$$A^a(\mathbf{q}) = i \sum_{\lambda\alpha} S_{\alpha,a}^\lambda \sqrt{\omega_a} (\mathbf{I}_\alpha^\lambda + \mathbf{J}_\alpha^\lambda) \quad (43)$$

are functions of the set of dimensionless normal coordinates \mathbf{q} . The atomic axial tensor $[\mathbf{I}_\alpha^\lambda(\mathbf{q}) + \mathbf{J}_\alpha^\lambda(\mathbf{q})]$ can be Taylor expanded in displacements from the equilibrium geometry. Truncating the expansion after second order the operator becomes

$$\mathbf{m}_{OO} = \mathbf{m}_{OO}^{(0)} + \mathbf{m}_{OO}^{(1)} + \mathbf{m}_{OO}^{(2)}, \quad (44)$$

where the zeroth-, first-, and second-order terms are

$$\mathbf{m}_{OO}^{(0)} = \sum_a A^a p_a, \quad (45)$$

$$\mathbf{m}_{OO}^{(1)} = \sum_{ab} A_{ab}^a q_b p_a, \quad (46)$$

$$\mathbf{m}_{OO}^{(2)} = \frac{1}{2} \sum_{abc} A_{bc}^a q_b q_c p_a. \quad (47)$$

The expansion coefficients A^a , A_{ab}^a , and A_{bc}^a are the zeroth-, first-, and second-order derivatives of the AAT surface $A^a(\mathbf{q})$ with respect to the dimensionless normal coordinates at the equilibrium geometry.

Applying contact transformation formulas through second order to the magnetic dipole moment operator in Eq. (44) gives

$$\bar{\mathbf{m}}_{OO} = \bar{\mathbf{m}}_{OO}^{(0)} + \bar{\mathbf{m}}_{OO}^{(1)} + \bar{\mathbf{m}}_{OO}^{(2)}. \quad (48)$$

The zeroth-, first-, and second-order terms of this operator have the forms

$$\bar{\mathbf{m}}_{OO}^{(0)} = \mathbf{m}_{OO}^{(0)}, \quad (49)$$

$$\bar{\mathbf{m}}_{OO}^{(1)} = \mathbf{m}_{OO}^{(1)} + i[S_1, \mathbf{m}_{OO}^{(0)}], \quad (50)$$

$$\begin{aligned} \bar{\mathbf{m}}_{OO}^{(2)} = & \mathbf{m}_{OO}^{(2)} + i[S_1, \mathbf{m}_{OO}^{(1)}] - \frac{1}{2}[S_1, [S_1, \mathbf{m}_{OO}^{(0)}]] \\ & + i[S_2, \mathbf{m}_{OO}^{(0)}], \end{aligned} \quad (51)$$

where the Hermitian operators S_1 and S_2 are given as

$$S_1 = \sum_{abc} S^{abc} p_a p_b p_c + S_{ac}^b q_a p_b q_c, \quad (52)$$

$$\begin{aligned} S_2 = & \sum_{abcd} \frac{1}{2} S_d^{abc} (p_a p_b p_c q_d + q_d p_a p_b p_c) \\ & + \frac{1}{2} S_{abc}^d (q_a q_b q_c p_d + p_d q_a q_b q_c). \end{aligned} \quad (53)$$

The coefficients S^{abc} , S_{ac}^b , S_d^{abc} , and S_{abc}^d are as given in Ref. 36.

The explicit form of the contact transformed magnetic dipole moment operator Eq. (48) is obtained by inserting Eqs. (45)–(47) and (52) and (53) into Eqs. (49)–(51)

$$\bar{\mathbf{m}}_{OO}^{(0)} = \sum_a \mathbf{A}^a p_a, \quad (54)$$

$$\bar{\mathbf{m}}_{OO}^{(1)} = \sum_{ab} \mathbf{A}_{ab}^b q_a p_b - \sum_{abc} \mathbf{A}_{ac}^c (q_a p_b + p_b q_a), \quad (55)$$

$$\bar{\mathbf{m}}_{OO}^{(2)} = \sum_{abc} \mathbf{B}^{abc} p_a p_b p_c + \mathbf{B}_{ab}^c q_a q_b p_c + i \sum_a \mathbf{C}_a q_a, \quad (56)$$

with

$$\mathbf{B}^{abc} = \sum_d (3\mathbf{A}_d^c S^{abd} - \mathbf{A}^d S_d^{abc}) - \sum_{de} (3\mathbf{A}^e S^{abd} S_{de}^c), \quad (57)$$

$$\begin{aligned} \mathbf{B}_{ab}^c = & \frac{1}{2} \mathbf{A}_{ab}^c + \sum_d (\mathbf{A}_d^c S_{ab}^d - 2\mathbf{A}_b^d S_{ad}^c - 3\mathbf{A}^d S_{abd}^c) \\ & + \sum_{de} (2\mathbf{A}^e S_{ad}^c S_{be}^d - \mathbf{A}^e S_{ab}^d S_{de}^c), \end{aligned} \quad (58)$$

$$\mathbf{C}_a = \sum_{bc} (\mathbf{A}_a^b S_{bc}^c + 3\mathbf{A}^b S_{abc}^c) - \sum_{bcd} \mathbf{A}^d S_{ad}^b S_{bc}^c. \quad (59)$$

According to the general theory of contact transformations the magnetic dipole transition moment in Eq. (28) correct to second order can be obtained from the zeroth-order vibrational basis $|\chi_{On}^{(0)}\rangle$ by substituting \mathbf{m}_{OO} in Eq. (28) with $\bar{\mathbf{m}}_{OO}$

$$\mathbf{m}_{On,Om} = \langle \chi_{Om}^{(0)} | \bar{\mathbf{m}}_{OO} | \chi_{On}^{(0)} \rangle - \langle \chi_{On}^{(0)} | \bar{\mathbf{m}}_{OO} | \chi_{Om}^{(0)} \rangle. \quad (60)$$

For fundamental transitions, the contact transformation expression simplifies

$$\begin{aligned} \mathbf{m}_{Og,0e}(\nu_a, 0 \rightarrow 1) \\ = i\sqrt{2} \mathbf{A}^a + \frac{i}{\sqrt{2}} \sum_b (\mathbf{B}^{abb} + \mathbf{B}^{bab} + \mathbf{B}^{bba} + \mathbf{B}_{bb}^a). \end{aligned} \quad (61)$$

The right-hand side of Eq. (61) involves zeroth-, first-, and diagonal second-order derivatives of the AAT surface. Notice that off-diagonal second order derivatives (i.e., A_{bc}^a with $b \neq c$) does not enter.

IV. CALCULATIONS

We have previously calculated anharmonic corrections to vibrational frequencies and infrared intensities of *trans*-2,3-dideuteriooxirane.³⁶ Most results of the previous study are reused to obtain the anharmonic corrections to the vibrational rotatory strength presented here.

Calculations were carried out at the SCF and MP2 level using the TZ2P basis set of Dunning.³⁷ The molecular Hessians, dipole derivatives [also known as atomic polar tensors (APT)], and equilibrium geometries were obtained using the CADPAC suite of programs.³⁸ AATs were calculated using London atomic orbitals [also known as gauge invariant atomic orbitals (GIAO)] only at the SCF level using the HERMIT/SIRIUS/ABACUS suite of programs.³⁹ As in our previous work the quartic force fields and quadratic expansions of the APT and now the AAT surfaces were computed by a least-squares fitting of values from 23 geometries (16 of *a* symmetry and 7 of *b* symmetry) selected to give a robust determination of the fitted constants (for more details see Refs. 33 and 35).

TABLE I. Vibrational frequencies ν [cm^{-1}] and rotatory strengths [$10^{-44} \text{esu}^2 \text{cm}^2$] of *trans*-2,3-dideuteriooxirane evaluated using the TZ2P basis set.

Mode		Vibrational frequencies			Rotatory strengths					
		Anharmonic			Double-harmonic			Anharmonic		
		SCF	MP2	Expt.	SCF	MP2	MP2 ^a	SCF	MP2	Expt. ^b
1	<i>b</i>	3179	3078	3028	27.2	18.1	22.8	29.1	20.2	11.4
2	<i>a</i>	3177	3091	3015	-23.6	-19.6	-24.4	-25.0	-22.0	-8.9
3	<i>a</i>	2358 ^c	2294	2254	13.1	10.1	12.7	10.2 ^c	9.3	12.1
4	<i>b</i>	2352	2279 ^c	2240	-13.0	-8.7	-11.2	-11.6	-6.5 ^c	-10.4
5	<i>a</i>	1526	1406	1397	-11.4	-8.5	-8.3	-10.6	-7.1	(-15)
6	<i>b</i>	1451	1351	1339	-1.9	-1.1	-1.3	-1.7	-1.1	(-2.5)
7	<i>a</i>	1336	1234	1235	14.3	11.1	10.9	14.4	11.3	24.1
8	<i>a</i>	1240	1122	1112	10.3	-5.3	-6.3	7.9	-9.1	-4.9
9	<i>b</i>	1225	1099	1106	7.8	10.5	10.1	7.7	8.8	11.1
10	<i>a</i>	1059	955	961	-45.7	-28.1	-28.2	-42.5	-25.3	-29.0
11	<i>b</i>	1012	912	914	0.8	-3.7	-3.7	0.0	-3.1	-6.2
12	<i>a</i>	959	864	885	7.4	8.8	8.0	5.8	10.0	(5)
13	<i>b</i>	924	807	817	0.2	1.1	1.7	1.3	1.2	(+)
14	<i>a</i>	820	758	754	13.7	10.3	11.8	14.0	9.8	
15	<i>b</i>	708	648	673	1.2	0.3	0.0	1.0	1.3	

^aVD3P basis, Ref. 22.^bReference 28, in CS_2 solution ($\nu_1 - \nu_4$ modes in C_2Cl_4 solution). Values in parentheses were estimated from the relative intensities in the gas-phase spectrum.^cAffected by the resonances.

In our partly MP2 calculation of vibrational rotatory strength the equilibrium geometry, the potential energy surface, and the APT surface were obtained at the MP2 level. The AAT surface was calculated at the SCF level but some correlation was introduced using the distributed origin (DO) electronic AATs⁴⁰ obtained as

$$\mathbf{I}_\alpha^\lambda = \mathbf{I}_\alpha^\lambda(\text{SCF}) - \frac{i}{4} \mathbf{Y}_\lambda \times \left(\frac{\partial \boldsymbol{\mu}_{OO}^e(\text{SCF})}{\partial R_{\lambda\alpha}} - \frac{\partial \boldsymbol{\mu}_{OO}^e(\text{MP2})}{\partial R_{\lambda\alpha}} \right), \quad (62)$$

where \mathbf{Y}_λ is the vector from the gauge origin to the center of nucleus λ and SCF and MP2 designate the level of theory used in the evaluation of individual terms. The use of DO AATs in this partly SCF and partly MP2 calculation ensures that the vibrational rotatory strengths are gauge origin independent. Results from these calculations are referred to as MP2 results. In the SCF calculations the use of London atomic orbitals ensure the vibrational rotatory strengths to be gauge origin independent.^{25,27,41}

The contact transformation calculations were carried out with the newly developed program CONTRA95 which has previously been used also for the calculations of the anharmonic contributions to the dipole strengths.^{36,42} The program allows evaluation of matrix elements of any polynomial operator expressed in terms of dimensionless normal coordinates and conjugated momentum operators.

To judge the influence of higher order anharmonic terms for the C-H stretchings further calculations were performed for these two modes. Two-dimensional (q_1, q_2) variational and contact transformation calculations were carried out for quartic and in the case of the variational calculations also for a sextic representation of the vibrational Hamiltonian. Harmonic oscillator product basis sets were employed. For the sextic representation, the corresponding two-dimensional APT and AAT surfaces were obtained by fitting to fourth-

order polynomials. The displacement points were selected to cover the potential energy surface up to 5000 cm^{-1} .

V. RESULTS AND DISCUSSIONS

The calculated anharmonic vibrational frequencies and rotatory strengths are listed in Table I. For comparisons Table I also contains the experimental results and rotatory strengths obtained in the double-harmonic approximation. The anharmonic corrections for the rotatory strengths are small for all modes compared to the large discrepancies between SCF and also MP2 double-harmonic results and experiment for modes 1, 2, and 7.²² The remaining discrepancies between experimental and theoretical results may arise from the use of incomplete basis sets, the incomplete inclusion of electronic correlation especially in the AATs which are only considered at the SCF level, incomplete handling of anharmonicity, and errors in the experimental results including solvent effects. To get some more insight into the possible theoretical errors we give in Table II individual contributions due to correlation, enlargement of basis set, and anharmonicity. For comparisons we also report in Table II the difference between experiment and anharmonic MP2 results. The largest change in rotatory strength result from inclusion of electronic correlation (MP2) and is $17.6 \times 10^{-44} \text{esu}^2 \text{cm}^2$ for mode 10; in average (using the norm of the individual changes) the change is $5.0 \times 10^{-44} \text{esu}^2 \text{cm}^2$. For comparison the numerically largest experimental rotary strength is $-29.0 \times 10^{-44} \text{esu}^2 \text{cm}^2$. The effect of MP2 is thus very significant for the rotatory strengths and they may be expected to change further using higher levels of correlation. The largest basis set used in double-harmonic MP2 rotatory strengths calculations on *trans*-2,3-dideuteriooxirane is the VD3P basis set.²² Comparing the TZ2P double-harmonic MP2 rotatory strengths with the VD3P results gives a maximum change for the C-H

TABLE II. Differences of vibrational rotatory strengths for *trans*-2,3-dideuteriooxirane calculated at various levels of theory and experimental results. Units in 10^{-44} esu² cm².

Mode	$\Delta_{\text{Correlation}}^a$	Δ_{Basis}^b	$\Delta_{\text{Anharmonicity}}^c$	$\Delta_{\text{Experiment}}^d$
1 <i>b</i>	-9.1	4.7	2.1	-8.8
2 <i>a</i>	4.0	-4.8	-2.4	13.1
3 <i>a</i>	-3.0	2.6	-0.8	2.8
4 <i>b</i>	4.3	-2.5	2.2	-3.9
5 <i>a</i>	2.9	0.2	1.4	-7.9
6 <i>b</i>	0.8	-0.2	0.0	-1.4
7 <i>a</i>	-3.2	-0.2	0.2	12.8
8 <i>a</i>	-15.6	-1.0	-3.8	4.2
9 <i>b</i>	2.7	-0.4	-1.7	2.3
10 <i>a</i>	17.6	-0.1	2.8	-3.7
11 <i>b</i>	-4.5	0.0	0.6	-3.1
12 <i>a</i>	1.4	-0.8	1.2	-5.0
13 <i>b</i>	0.9	0.6	0.1	
14 <i>a</i>	-3.4	1.5	-0.5	
15 <i>b</i>	-0.9	-0.3	1.0	

^aObtained as $R(\text{MP2}) - R(\text{SCF})$ where the rotatory strengths are calculated in the double harmonic approximation using the TZ2P basis set.

^bObtained as $R(\text{VD3P}) - R(\text{TZ2P})$ where the rotatory strengths are calculated at the MP2 level of theory using the double harmonic approximation. The $R(\text{VD3P})$ results are taken from Ref. 22. Notice that London atomic orbitals are used in the calculation of $R(\text{TZ2P})$ while conventional orbitals are used for $R(\text{VD3P})$. However, for the large VD3P basis set previous calculations in Ref. 41 show that rotatory strength obtained with and without the use of London atomic orbitals are very alike.

^cObtained as $R(\text{anharmonic}) - R(\text{double-harmonic})$ where the rotatory strengths are calculated at the MP2 level of theory using the TZ2P basis set.

^dObtained as $R(\text{experiment}) - R(\text{anharmonic})$ where the calculated rotatory strengths are at the MP2 level of theory using the TZ2P basis set.

and C–D stretching modes of -4.8×10^{-44} esu² cm². For the other modes the average discrepancy (using the norms) is only 0.5×10^{-44} esu² cm². Extending the basis set beyond the VD3P level might have some effect for the C–H and C–D stretchings modes but is expected to be negligible for other modes.

At the MP2 level the largest anharmonicity correction using the quartic approximation is -3.8×10^{-44} esu² cm². In average the contribution (based on norm values) is 1.4×10^{-44} esu² cm². These contributions are rather small compared to the discrepancies between the anharmonic results

and experiment. The maximum of these discrepancies is 13.1×10^{-44} esu² cm² (for the second C–H stretch) and the average value using the norms is 5.8×10^{-44} esu² cm². The influence of higher order anharmonic terms for the C–H stretchings can be estimated from the SCF results presented in Table III. Comparing the results obtained in the two-dimensional model and in the full dimension using the contact transformation show that the two-dimensional model gives very reliable results. Both frequencies, dipole strengths, and rotatory strengths agree very well. Variational calculations using a two-dimensional model and a quartic representation of the vibrational Hamiltonian give results that agree well with the two-dimensional contact transformation results for both frequencies, dipole strengths, and rotatory strengths. Variational calculations using quartic and sextic representations of the vibrational Hamiltonian also agree well proving that little is gained from going beyond the quartic approximation for these modes. Combining these observations it is clear that only absolutely minor corrections to the C–H rotatory strengths can be expected in calculations where anharmonicities are calculated to higher accuracy than in this work.

VI. CONCLUSION

Theoretical expressions have been derived for the vibrational rotatory strength that can be used to calculate anharmonic contributions using *ab initio* electronic structure calculations. As in previous *a priori* theories^{2,3} the expression is based on a magnetic dipole transition moment which incorporates non-Born–Oppenheimer effects to first order. In contrast to the previous derivations the magnetic dipole transition moment is derived without using the harmonic or the Condon approximations. The obtained expression for the vibrational rotatory strength is gauge origin independent and it reduce to previous expressions in the double-harmonic approximation. Second-order contact transformation theory is used to obtain the magnetic dipole transition moment. The resulting expressions require that zeroth-, first-, and diagonal second derivatives of the AAT surface are calculated at the equilibrium geometry. Off-diagonal second derivatives are

TABLE III. Anharmonic frequencies [cm^{-1}], dipole strengths [10^{-40} esu² cm²], and rotatory strengths [10^{-44} esu² cm²] for ν_1 and ν_2 modes (CH stretchings) of *trans*-2,3-dideuteriooxirane calculated at the SCF/TZ2P level. Contact transformations (CT) were carried out for full- and two-dimensional models, variational calculations for the two-dimensional model using 10×10 harmonic oscillator product basis. H_4 denotes a quartic representation, and H_6 denotes a sextic representation of the vibrational Hamiltonian.

Mode	CT		Variational	
	full- H_4	2D- H_4	2D- H_4	2D- H_6
Frequencies				
1 <i>b</i>	3179	3192	3222	3196
2 <i>a</i>	3177	3187	3219	3191
Dipole strengths				
1 <i>b</i>	65.4	68.9	67.9	69.0
2 <i>a</i>	8.2	8.8	8.7	8.8
Rotatory strengths				
1 <i>b</i>	29.1	31.6	31.4	31.6
2 <i>a</i>	-25.0	-27.0	-26.8	-27.0

not needed. The required derivatives are obtained using single point calculations of the AATs. In addition to the equilibrium geometry point only two points are needed for each dimensionless normal coordinate. For *trans*-2,3-dideuteriooxirane symmetry further reduce the number of needed points.

Anharmonic corrections have been calculated for the vibrational rotatory strengths of *trans*-2,3-dideuteriooxirane. Double-harmonic results have previously shown large discrepancies to experiment for three out of the 15 vibrational modes. The two C–H stretching modes are among the modes with large discrepancies and it has been suggested that anharmonicity might be responsible for the large deviations. The calculations in this work show that the anharmonicity effects are small for all 15 modes including the C–H stretchings. A detailed analysis of anharmonicity beyond what is obtained using the second-order contact transformation show that the effects from higher order are negligible for the C–H stretchings. Anharmonicity therefore is *not* responsible for the discrepancies between double harmonic results and experiment. Other possible sources of errors are the use of incomplete basis sets and the fact that electronic correlation is included at a low level. The VD3P results are generally expected to be close to basis set convergence. Comparison of TZ2P and VD3P MP2 results have indicated that relatively small changes can be expected from extending the basis set beyond the VD3P basis set except for the C–H and C–D modes where some effect might be observed. The MP2 vibrational rotatory strengths are very different from the SCF results. It is therefore possible that more complete treatment of electronic correlation will have some significant effect, especially because the AATs are partly SCF tensors. Decisive conclusions about the possible basis set and electronic correlation convergence errors must await more elaborate calculations.

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