

The excitation scheme: A new method for calculation of vibrational circular dichroism spectra

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An alternate procedure for calculating vibrational circular dichroism is proposed. The method eliminates the need to solve the magnetically perturbed SCF equations which leads to an overall decrease in computer time. Instead, an expansion over electronic excited states is partially used to estimate the molecular response to the magnetic field and nuclear displacements. A rigid orbital approximation is used for the electronic states. The rotational strengths obtained in this manner are compared to original experimental data for camphor and α -pinene, and previous calculations on propylene oxide and oxirane. In all cases good agreement of simulated spectral intensities with experiment is observed. Although extensive approximations had to be adopted in the current implementation, the excitation scheme yields results superior to those obtained by the classical MFP or VCT formulations of VCD for camphor and α -pinene, whereas MFP/GIAO theory performs better in the case of oxirane. © 1998 American Institute of Physics. [S0021-9606(98)01321-X]

I. INTRODUCTION

The interpretation of vibrational circular dichroism spectra of medium-sized molecules is almost entirely based on *ab initio* calculations.¹⁻³ Although some empirical approaches are proposed and appear promising for peptides⁴ for example, the first principles techniques can be extended to molecules of almost any arbitrary size.^{5,6} Nevertheless, the limitations of quantum chemical procedures still determine the reliability and accuracy of theoretical modeling.

Although a correct theoretical description of the vibrational circular dichroism (VCD) phenomenon is not possible strictly using the Born-Oppenheimer (BO) approximation, VCD intensities can be obtained from conventional BO wave functions. This can be demonstrated most clearly on the magnetic field perturbation theory (MFP) of Stephens^{7,8} where only the electronic ground state derivatives are required. The MFP theory is implemented in CADPAC (Ref. 9) and GAUSSIAN (Ref. 10) program packages. For the older vibronic coupling theory¹¹ (VCT, implemented as the VCT90 program¹²) excited electronic states are required formally. However, these can be sufficiently approximated with singly excited states derived from the ground state. Approximate approaches, like localized molecular orbital theory (LMO),¹³ were devised but used less frequently. Comparative studies showed that MFP and VCT provide results of the same quality and that the results approach a common limit if a sufficiently large basis set and a high *ab initio* level of approximation are used.^{14,15} Computation of VCD with these theories is, however, severely limited by molecular size. Although VCT partially removes the difficulties associated with the handling of imaginary magnetic perturbation, its

current implementation requires the storage of the nuclear derivatives which is very demanding on computer disk space.

Here, we attempt to circumvent completely the solution of magnetically coupled HF equations¹⁶ or the hybrid HF-density functional theory (DFT) functionals.¹⁷ As shown lately for calculation of electric and magnetic polarizability tensors, this can be achieved by the proper excitation scheme (EXC), where the energies and excited wave functions are derived from the Hartree-Fock or Kohn-Sham (KS) orbitals.¹⁸ It has already been proven that these sum over state (SOS) methods can be used effectively in the DFT-based calculations of nuclear shielding tensors.¹⁹ Thus we feel that there is an enormous potential of this approach, since the DFT-SOS procedures can more easily be extended to bigger molecules than the conventional orbital post-HF theories and more complete bases can be used. We retain the abbreviation "EXC" for the current method in order to distinguish it from the VCT formalism, which can be also considered a SOS technique, unlike the MFP theory.

To test the results we chose the spectra of relatively nonpolar terpenes, camphor and α -pinene, as the main model systems, since their VCD can be reliably measured. Previous experiments^{1,2} as well as our trial measurements suggest that the VCD signal of nonpolar molecules is almost unchanged by the solvent, which justifies the comparison to *ab initio* modeling, where a molecule in vacuum is the natural target.

II. THEORY

A. Basic relations

VCD intensity of each harmonic vibrational transition i is proportional to the rotatory strength, R_i , given by

$$R_i = \hbar^2 \text{Im}[P_i \cdot M_i], \quad (1)$$

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where $P_{i\beta} = \sum_{\lambda} P_{\alpha\beta}^{\lambda} S_{\lambda\alpha,i}$ and $M_{i\beta} = \sum_{\lambda} M_{\alpha\beta}^{\lambda} S_{\lambda\alpha,i}$ are the atomic polar (APT) and atomic axial tensors (AAT), respectively, and \hbar is the Planck's constant. The tensors can be written in Cartesian or normal mode coordinates, since \mathbf{S} is the Cartesian to normal mode transformation matrix. Symbols α and β denote Cartesian components, sums run over all atoms λ , and the Einstein summation convention is used throughout this work, i.e., two coordinate indices occurring in a product are also summed over the x , y , and z axes. The atomic axial tensor becomes the main concern in calculating the VCD phenomenon. It can be decomposed into its nuclear and electronic parts, $\mathbf{M} = \mathbf{J} + \mathbf{I}$, where

$$J_{\alpha\beta}^{\lambda} = \frac{i}{4\hbar c} \varepsilon_{\alpha\beta\gamma} R_{\lambda\gamma}^0 Z_{\lambda} \quad (2)$$

and

$$(\text{MFP}) I_{\alpha\beta}^{\lambda} = \left\langle \frac{\partial n}{\partial R_{\alpha}^{\lambda}} \middle| \frac{\partial n}{\partial B_{\beta}} \right\rangle. \quad (3)$$

Symbol Z_{λ} denotes nuclear charge, \mathbf{R}_{λ}^0 is the equilibrium position of the nucleus λ , and c is the velocity of light. In Eq. (3), the nuclear derivative of the ground state electronic function n is overlapped with a derivative with respect to the magnetic field, \mathbf{B} . The derivatives are assumed to be estimated at the equilibrium positions of the nuclei and at the zero limit of the field. Although historically a SOS expression of the AAT based on perturbation expansions¹¹ preceded the discovery of Eq. (3), we use the MFP formula as a starting point for the derivations presented below. Originally implemented at the HF level,²⁰ the perturbation theory was recently extended to MP2 (Ref. 21) and DFT (Ref. 22) calculations.

From Eq. (3), alternate expressions for the tensor can be derived. Firstly, a sum over *all* eigenfunctions of the electronic Hamiltonian (H_e) is inserted, so that

$$I_{\alpha\beta}^{\lambda} = \sum_j \left\langle \frac{\partial n}{\partial R_{\alpha}^{\lambda}} \middle| j \right\rangle \left\langle j \middle| \frac{\partial n}{\partial B_{\beta}} \right\rangle. \quad (4)$$

It should be emphasized that the states n and j in Eqs. (3) and (4) are neither exact molecular states (as they would be if H_e were exact) nor any approximate basis-dependent model. They form a complete set, $1 = \sum_j |j\rangle\langle j|$. In addition, for such a system $\langle j | \partial n / \partial B_{\beta} \rangle = W_{jn}^{-1} \langle j | [H_e, \partial / \partial B_{\beta}] | n \rangle = W_{jn}^{-1} \langle j | m_{\beta} | n \rangle$ (Ref. 18) and we get

$$(\text{VCT}) I_{\alpha\beta}^{\lambda} = \sum_j \left\langle \frac{\partial n}{\partial R_{\alpha}^{\lambda}} \middle| j \right\rangle \frac{\langle j | m_{\beta} | n \rangle}{W_{jn}}, \quad (5)$$

where $W_{jn} = W_j - W_n$ is the energy difference between excited and ground molecular states, and m is the total electronic magnetic moment. For correct excited states Eqs. (3) and (5) give same results. As pointed out in the Introduction, the VCT relation allows one to avoid the relatively complicated implementation of the magnetic perturbations. Instead, a good representation of the space of the excited states has to be found. However, for practical calculations, the excited states can be approximated directly from Slater determinant by singly excited states without further orbital relaxation.¹² Thus, almost no extra computational time is required, if com-

pared with a single point SCF cycle. The post-HF extension using MP2 wave functions²³ improved only slightly the performance of the method.

B. The origin dependence

Neither VCT nor MFP can be used directly for computations on larger molecules where a rather incomplete basis set has to be used. In such a case, calculated rotatory strengths are strongly dependent on the origin of coordinates. The dependence can be removed either by introducing magnetic field dependent atomic orbitals²⁴ (gauge invariant AO, GIAO, in the MFP procedure), or by using a distributed origin gauge (DOG) transformation both in VCT and MFP. For the latter procedure, part of the AAT is calculated from APT using

$$I_{\alpha\beta}^{\lambda}(0) = I_{\alpha\beta}^{\lambda}(\lambda) + \frac{i}{4\hbar c} \varepsilon_{\beta\gamma\delta} R_{\gamma}^{\lambda} P_{\alpha\beta}^{\lambda}, \quad (6)$$

where $\mathbf{I}(0)$ and $\mathbf{I}(\lambda)$ are the AATs in the laboratory coordinate system, and in the system shifted to the equilibrium position of an atom λ , respectively, and $\varepsilon_{\beta\gamma\delta}$ is the antisymmetric permutation tensor. \mathbf{P} is calculated routinely at a higher level of approximation than \mathbf{I} ,²¹ which further increases the accuracy of the computations.

C. The excitation scheme

The method proposed here takes advantage of the generalized Hellmann-Feynman theorem which allows one to express also the first integral in Eq. (5) with only unperturbed wave functions, i.e., $\langle \partial n / (\partial R_{\alpha}^{\lambda}) | j \rangle = W_{jn}^{-1} \langle n | o_{\alpha}^{\lambda} | j \rangle$, where the gradient operator is

$$o_{\alpha}^{\lambda} = - \frac{\partial H}{\partial R_{\alpha}^{\lambda}} = \sum_{\mu \neq \lambda} \frac{Z_{\lambda} Z_{\mu} e^2 (R_{\alpha}^{\lambda} - R_{\alpha}^{\mu})}{|\mathbf{R}^{\mu} - \mathbf{R}^{\lambda}|^3} - \sum_i \frac{Z_{\lambda} e^2 (R_{\alpha}^{\lambda} - r_{i\alpha})}{|\mathbf{r}^i - \mathbf{R}^{\lambda}|^3};$$

e is the charge of electron, \mathbf{r}_i is the position vector of an electron i , and \mathbf{R}^{μ} denotes the equilibrium position of an atom μ . Note that the nuclear part of the gradient vanishes because of the orthogonality of the basis, $\langle j | n \rangle = 0$ for $j \neq n$. Thus the basic relation for the calculation of VCD in the excitation scheme becomes

$$(\text{EXC}) I_{\alpha\beta}^{\lambda} = \sum_{j \neq n} \frac{\langle n | o_{\alpha}^{\lambda} | j \rangle \langle j | m_{\beta} | n \rangle}{W_{jn}^2}. \quad (7)$$

Although the MFP, VCT and EXC relations are thus formally equal, results calculated with approximate models of electronic states and energies may be quite different. In this work, the states (for closed-shell systems) are approximated with the singly excited spin adapted Slater determinants,²⁵ $|j\rangle \equiv \Delta_{K>J}$. Then from Eq. (7) we get

$$I_{\alpha\beta}^{\lambda} = 2 \sum_{K, \text{occ}} \sum_{J, \text{virt}} \frac{\langle K | o_{\alpha}^{\lambda} | J \rangle \langle J | m_{\beta} | K \rangle}{W_{JK}^2}, \quad (8)$$

where $W_{JK} = \varepsilon_J - \varepsilon_K$

spectively, ε_K and ε_J are corresponding orbital energies, and $K_{JK}=(JK|JK)$ and $J_{JK}=(JJ|KK)$ are the usual exchange and Coulomb integrals, respectively. To match the relation (7) more closely, a configuration interaction would have to be considered, which we leave for future studies. The gradient and magnetic moment become one-particle operators,

$$O_{\alpha}^{\lambda} = -\frac{Z_{\lambda}e^2(R_{\alpha}^{\lambda}-r_{\alpha})}{|\mathbf{r}-\mathbf{R}^{\lambda}|^3}$$

and

$$M_{\alpha} = \frac{i\hbar e}{2m_e c} \varepsilon_{\alpha\beta\gamma} r_{\beta} \nabla_{\gamma},$$

m_e is the mass of electron.

The distributed origin gauge can be used in the excitation scheme if an analogous expression is written for the electronic part of the APT, $\mathbf{P}(e)$:

$$P(e)_{\alpha\beta}^{\lambda} = 4 \sum_{K, \text{occ}} \sum_{J, \text{virt}} \frac{\langle K|O_{\alpha}^{\lambda}|J\rangle \langle J|U_{\beta}|K\rangle}{W_{JK}} \quad (9)$$

and its gradient representation, $\mathbf{V}(e)$,

$$V(e)_{\alpha\beta}^{\lambda} = \frac{4e\hbar^2}{m} \sum_{K, \text{occ}} \sum_{J, \text{virt}} \frac{\langle K|O_{\alpha}^{\lambda}|J\rangle \langle J|\nabla_{\beta}|K\rangle}{W_{JK}^2}, \quad (10)$$

where μ is the total and \mathbf{U} the one-electron dipole moment, $\mu = \sum_i \mathbf{U}_i$. Then the local electronic AAT becomes

$$I_{\alpha\beta}^{\lambda}(\lambda) = I_{\alpha\beta}^{\lambda}(0) - \frac{i}{4\hbar c} \varepsilon_{\beta\gamma\delta} R_{\gamma}^{\lambda} V(e)_{\alpha\beta}^{\lambda}. \quad (11)$$

A direct use of Eq. (6) with $\mathbf{P}(e)$ defined in Eq. (9) and $\mathbf{I}(\lambda)$ from Eq. (11) would already lead to origin-independent results. However, APTs calculated with approximate wave functions according to Eq. (9) are less accurate than if calculated using the coupled HF or analogous perturbational theory and does not obey the most obvious translational and rotational rules.²⁶ Thus, in Eq. (6), we use the APT tensor derived from the ground state electric field perturbed wave function as given by the Gaussian output, for example.

Although the SOS (EXC) model presented above is justified for calculations based on the HF rigid-orbital approximation, the replacement of the molecular orbitals by the Kohn-Sham orbitals is based on an empirical experience only. As discussed previously, density functional theory is not a self-consistent variational method.¹⁹ Nevertheless, several approximate models of the excited states yielding useful results can be found.^{18,19} The excitation energies W_{JK} , for example, can be calculated as the difference of the Kohn-Sham orbital energies ($\varepsilon_j - \varepsilon_K$), or the exchange term can be included ($\varepsilon_j - \varepsilon_K + 2K_{JK}$), or the HF expression ($\varepsilon_j - \varepsilon_K + 2K_{JK} - J_{JK}$) can be recalculated for KS orbitals. We found the last approach most rewarding for calculation of polarizabilities, while the first approximation is computationally least demanding. The first approach resembles exact solutions of coupled Kohn-Sham equations for the magnetic field [for W_{jn} and $\partial n/\partial \mathbf{B}$ in Eqs. (5) and (6)] but not for the nuclear displacements [W_{jn} and $\partial n/\partial \mathbf{R}$ in Eqs. (8)], since only the magnetic perturbation does not change the electron density. An alternate DFT formalism for modeling of the

excited states may be based on the time-dependent adiabatic approximation,²⁷ which is, however, currently inaccessible for us.

D. The super-excitation scheme

By the expansion into the excited state space, the computationally expensive derivatives of the wave function with respect to the nuclear displacements and the magnetic field were completely avoided. Similarly, the dependence of magnetic properties on the gradient of the wave function can be avoided by another SOS expansion and using the hypervirial relation for the gradient,

$$\langle j|\nabla_{\delta}|n\rangle = -\frac{mW_{jn}}{\hbar^2} \langle j|r_{\delta}|n\rangle.$$

Thus another representation of the AAT can be obtained:

$$\begin{aligned} \text{(SUPER)} \quad I_{\alpha\beta}^{\lambda} = & -\frac{ie}{2\hbar c} \varepsilon_{\beta\gamma\delta} \sum_i \sum_{j\mathbf{8}\neq n} \sum_{j'\neq n} \frac{W_{j\mathbf{8}n}}{W_{jn}^2} \\ & \times \langle n|o_{\alpha}^{\lambda}|j\rangle \langle j|r_{\gamma}^i|j\mathbf{8}\rangle \langle j\mathbf{8}|r_{\delta}^i|n\rangle. \end{aligned} \quad (12)$$

The lack of the gradient may *in principle* decrease basis set dependence and remove the origin dependence of the results. However, for the approximate model of the excited states used here the error stemming from the insertion of the second closure formula outweighs these advantages, as shown for the examples below. Nevertheless, we consider Eq. (12) an interesting representation of the AAT from the theoretical point of view and, as shown elsewhere,²⁸ a special case of the gradient-independent formula can be used for reliable computations of the VCD even for bigger molecules.

III. COMPUTATIONS

The geometries of the trial molecules (water, camphor, α -pinene, propylene oxide and oxirane) were optimized and the harmonic force fields and atomic polar tensors calculated with the Gaussian set of programs at the B3LYP/631G** (6-311G** basis for oxirane) level. The molecular orbital coefficients and energies were read from the GAUSSIAN 94 output with our supplementary programs ("RoA"), and the necessary one- and two-electron integrals and Coulomb and exchange terms were recalculated. A different basis was used for the AAT calculation than for the force field as indicated later. Finally, the atomic axial tensors were combined with the Gaussian APTs according to the distributed origin gauge, and the dipolar and rotatory strengths were obtained using the DFT force field.

IV. EXPERIMENT

The description of our VCD spectrometer can be found elsewhere.²⁹ The spectra of camphor were measured for solutions in CCl_4 , and spectra of α -pinene were measured in CCl_4 and CS_2 . A negligible influence of the solvent on the spectra was observed. The chemicals were purchased from Aldrich and used without further purification. NaCl cells with an optical path of 0.15 mm were used. A total of 5000 scans were accumulated for the VCD measurements with a

TABLE I. The dependence of the local atomic axial tensor on the size of basis set. Calculation for the H₂O molecule (B3LYP/6-31G** geometry, in the *yz* plane, *z* as the C₂ axis). Values given as calculated by SUPER/EXC/MFP theories; atomic units used.

Tensor Component ^a	631G (13 bf)	631G** (25 bf)	631GE (43 bf)	AUG-cc-VTZ (105 bf)
<i>H_{x,y}</i>	-0.010/-0.002/0.036	-0.139/-0.066/-0.043	-0.137/-0.069/-0.084	-0.185/-0.119/-0.093
<i>H_{x,z}</i>	-0.014/-0.005/-0.051	0.196/0.086/0.063	0.198/0.098/0.121	0.268/0.171/0.136
<i>H_{y,x}</i>	-0.021/-0.041/-0.035	0.113/0.018/0.030	0.108/0.043/0.070	0.138/0.071/0.077
<i>H_{z,x}</i>	-0.167/-0.111/0.000	-0.317/-0.189/-0.094	-0.288/-0.137/-0.145	-0.379/-0.235/-0.153
<i>O_{x,y}</i>	0.098/-0.935/-0.070	0.225/-0.57/0.087	0.259/0.027/0.168	0.385/0.059/0.186
<i>O_{y,x}</i>	-0.195/0.743/0.124	-0.305/0.37/-0.058	-0.306/-0.006/-0.138	-0.45/-0.029/-0.154

^a($\lambda\alpha, \beta$), where α is a coordinate of the atom λ , β is the field index.

resolution of 4 cm⁻¹. The rotatory strengths were obtained by a standard analysis of experimental spectra.¹⁵

V. RESULTS AND DISCUSSION

A. Basis set dependence

Although calculations on bigger molecules with a rather incomplete basis set are the primary target of VCD simulations, we chose the water molecule to test the method with respect to its convergence towards the HF limit. In Table I the local [viz. Eq. (7)] AATs are listed as calculated with the MFP theory (by the CADPAC 5 program), the excitation scheme [EXC, Eq. (11)], and the super-excitation procedure [SUP, Eq. (18)]. The usual definitions of the basis functions are used: the 631GE basis from CADPAC which has two sets of *d*-orbitals for heavy atoms, and the AUG-cc-VTZ basis of Gaussian which includes two sets of *f* orbitals on oxygen. As apparent in Table I, the AATs converge rather slowly with the basis set size. The 631G basis is quite insufficient, since the values of the AATs are generally small and their signs are not reliable compared with the most advanced AUG-cc-VTZ calculation. For the 631G** basis, which would be the most appropriate choice for a larger molecule, signs of the tensor components are mostly correct. The MFP theory appears to converge most rapidly and the EXC method leads to qualitatively similar results. For example, the MFP value for the AUG-cc-VTZ basis of the (*O_{x,y}*) component is 0.186, which is only by about 10% higher than the MFP value for the 631GE basis, 0.168. The EXC values for this component differ by about 50% for these two bases, namely 0.059 and 0.027. The difference between MFP and EXC is smaller, however, for most of the other components. The SUP scheme largely overestimates the AAT components, which can apparently make up for the inadequacies of the basis set, since the signs are reproduced correctly except for the smallest basis. However, we do not consider the super-excitation approach viable for bigger molecules at this stage.

B. Camphor and α -pinene

Rotational strengths for the VCT, MFP, and EXC theories (R_{VCT} , R_{MFP} , and R_{EHF} , respectively) calculated for camphor with the B3LYP/6-31G** force field and HF/6-31G local AAT are compared with experiment in Table II. The frequencies were scaled uniformly by a factor of 0.9752. Apparently, the EXC approach is quite superior to the VCT and MFP calculations for this molecule: on the average

VCT, MFP and EXC rotatory strengths are equal to 20%, 24%, and 43% of the observed values, respectively, see coefficient *a* in the table. R_{EDF} strengths were also calculated by the EXC method using the B3LYP/6-31G wave function (Kohn-Sham determinant) for local AATs; all energies were recalculated in Eq. (12) with this wave function. As apparent, the DFT values (R_{EDF}) are qualitatively comparable to the HF calculations (R_{EHF}), matching the experimental values with similar accuracy. The last set of rotatory strengths, R_{EDF^*} , was obtained consistently by the EXC scheme at the B3LYP/6-31G** level (used for the force field, APTs and AATs). In this case, due to the limitations of our program, the Coulomb and exchange terms in Eq. (12) were neglected and the orbital energies replaced with Kohn-Sham orbital energies from the Gaussian output. This approach led to the best approximation of experimental rotatory strengths, reproducing the observed experimental intensities to within 53% of the average. A larger value of the standard error ($\delta=75$ cm⁻¹) results from an overall increase of the calculated VCD signal and may be accounted for by an imperfect assignment of experimental data. For example, the experimental rotatory strength for mode 53 was tentatively determined as negative, which does not correspond to the calculation. However, modes 51–53 are not resolved and thus their individual contributions to this value are unknown. For individual modes, the limited accuracy of the force field as well as a low resolution of experimental bands introduce almost unpredictable errors in such a comparison. In addition, transitions especially in the poorly resolved higher frequency region (modes 51–59) can be affected by anharmonicities. Nevertheless, the overall success of the modeling is evident.

As a next test molecule we chose α -pinene. Recently, we have used the B3LYP/6-31G** force field to model its Raman optical activity (ROA) spectrum.³⁰ Unlike for ROA, the absolute experimental intensities are available for VCD, so that the adequacy of the calculations can be better judged. The bicyclic structure of α -pinene is even more rigid than for camphor, due to the four-member ring and the double bond in the hexene ring of the former. As shown below, this chemical difference has little effect on the overall properties of the VCD signal of the two compounds. We did not find any significant changes in dipole and rotatory strengths between the measurements in the CCl₄ and CS₂ solvents. In Table III we list the experimental values for the CCl₄ solution, since the CS₂ spectra have a slightly worse S/N ratio. Because of possible band overlapping, the error for the ex-

TABLE II. Comparison of calculated and experimental rotatory strengths for(1R)-(+)-Camphor [in 10^{-9} Debye 2]: R_{VCT} , R_{MFP} and R_{EHF} - the VCT, MFP and EXC methods, respectively, all at the HF/6-31G level for AAT; R_{EDF} - the EXC calculation with B3LYP/6-31G for AAT; $R_{\text{EDF}*}$ - the EXC method with B3LYP/6-31G** for AAT, Kohn-Sham MO energies. Calculated (ω_{CAL} , B3LYP/6-31G**, scaled by 0.9752) and experimental (ω_{EXP}) frequencies in cm^{-1} . Symbols a and δ denote the coefficient and the standard deviation, respectively, for the fit $R_{\text{CAL}} = a \cdot R_{\text{EXP}}$.

#	ω_{CAL}	ω_{EXP}	R_{VCT}	R_{MFP}	R_{EHF}	R_{EDF}	$R_{\text{EDF}*}$	R_{EXP}
59	1795	1747	132	147	386	491	495	
58	1504	1480	-21	-20	-39	-40	-47	3
57	1492	1470	93	96	162	164	214	200
56	1488		9	10	15	16	17	
55	1476		-16	-5	-41	-41	-56	
54	1472	1454	51	60	77	87	102	102
53	1467	1448	44	52	119	136	161	-46
52	1462		-12	-12	-32	-31	-37	
51	1458		-15	-13	-42	-48	-40	
50	1434	1417	-6	-8	-59	-61	-94	-50
49	1404	1390	-46	-48	-86	-84	-97	-96
48	1388	1376	15	20	30	38	34	50
47	1383	1372	-10	-10	-26	-30	-19	-20
46	1320	1324	69	73	55	55	48	149
45	1305	1278	-25	-27	-156	-148	-221	-152
44	1299	1294	-10	-5	30	35	55	
43	1273	1276	-15	-16	38	46	46	37
42	1245	1246	89	97	209	197	266	419
41	1239	1234	4	7	27	26	37	
40	1220	1216	50	48	2	4	-32	3
39	1197	1198	-85	-99	-102	-116	-107	-123
38	1189	1189	7	-3	-3	-10	5	
37	1161	1166	57	71	112	126	174	222
36	1145	1151	-32	-47	-53	-71	-64	-121
35	1120	1128	52	68	105	115	148	64
34	1093	1093	-52	-78	74	54	140	-37
33	1073	1079	-75	-133	-16	-55	-21	19
32	1033	1045	-69	-106	-180	-149	-219	-715
31	1014	1021	-12	57	-92	-63	-23	-135
30	1007	1010	-16	-5	-68	-57	-84	97
29	978	985	-6	-8	-4	-6	-1	-47
28	941	952	-3	-8	-34	-29	-75	35
27	937	984	-59	-68	-134	-139	-180	-162
26	923	935	44	48	67	52	116	148
25	920	925	98	121	197	205	223	356
24	900	912	-68	-86	-137	-159	-120	-165
23	849	862	-37	-49	-63	-60	-78	-66
22	837	854	-73	-112	-127	-154	-169	-216
21	817	825	-11	-15	-18	-17	-19	
a			0.20	0.24	0.44	0.43	0.53	
δ			35	47	54	59	75	

perimental rotatory strengths cannot be easily estimated, but are not likely to exceed 10% in most cases (20% for the weakest observed bands). Unlike for camphor, the VCT, MFP and EXC procedures led to approximately the same values for rotatory strengths (cf. coefficients a in Table III for R_{VCT} , R_{MFP} and R_{EHF}). The EXC scheme, however, can be used with a bigger basis set even with our computer limitations, substantially improving the agreement (see the values of $R_{\text{EDF}*}$). The VCD spectra simulated by the three approaches and the observed spectrum are plotted in Fig. 2. VCT theory seems to fail to reproduce the signals of modes 37–41 (region around 1210 cm^{-1}). In this interval, however, it is not clear whether the accuracy of the force field is at fault because of overlapping bands, which in VCD can lead to subtraction of positive and negative bands. As can be seen

in Table III, VCT, MFP and EXC predicted same signs of rotatory strengths for most transitions in the mid *IR* region, and more differences can be observed in the C-H stretching region (modes 57–72), presently not accessible with our current instrumentation.

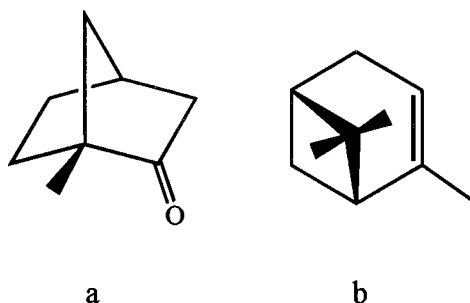
C. Propylene oxide and oxirane

For these two molecules we compared the performance of the EXC and SUPER schemes to previous MFP/SCF (propylene oxide)³¹ and DFT/GIAO (oxirane)³² calculations.

Rotatory strengths for propylene oxide are listed in Table IV. The C-H stretching region is omitted because of anharmonic effects that may be expected in this region. Of the 12 experimentally determined rotatory strengths, the

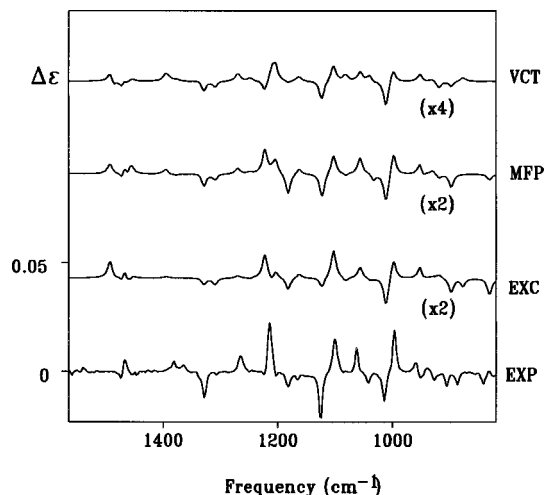
TABLE III. Rotatory strengths for α -pinene. Symbols and units analogous to those in Table II, calculated frequencies scaled by 0.9736, experimental frequencies obtained from the ROA spectra (Ref. 30) marked by R . D_{CAL} and D_{EXP} , the calculated (B3LYP/6-31G**) and experimental dipole strengths [10^{-5} Debye²]. Possible different mode ordering for experiment and calculation indicated by an asterisk in the first column.

Mode	ω_{CAL}	ω_{EXP}	D_{CAL}	D_{EXP}	R_{VCT}	R_{MFP}	R_{EHF}	R_{EDF}	R_{EXP}
72	3076		358		10	15	-27	-54	
71	3063		265		-14	0	149	195	
70	3057		499		4	15	-55	-130	
69	3042		429		-20	-49	-52	-43	
68	3034		293		-24	34	-76	-36	
67	3014		644		65	129	54	55	
66	3006		84		1	5	21	41	
65	2998		458		59	119	-213	-381	
64	2987		584		6	-78	291	456	
63	2985		295		29	3	69	51	
62	2975		810		-3	68	-248	-444	
61	2958		721		-28	-108	124	215	
60	2951		286		52	109	0	-64	
59	2950		269		-68	-107	-18	19	
58	2939		425		33	33	37	1	
57	2927		615		-24	-45	18	17	
56	1687	1657	23	43	-5	-3	2	3	
55	1492	1485	89	1	19	43	73	109	
54	1485	1469	102	417	-12	-2	-9	-1	-38
53	1472	1458R	39		-13	-33	-24	-33	
52	1467	1454	102		8	53	50	61	58
51	1463	1446	61	751	-8	-36	-27	-38	-15
50	1457	1442	64		3	37	-10	-18	-10
49	1452	1435	183	413	3	12	18	33	
48	1451	1417	48	9	-0	-5	-7	-10	
47	1395	1381	119	185	17	24	6	7	80
46	1389	1374	22	164	4	-6	1	1	30
45	1378	1364	163	300	3	-8	0	-5	
44	1339	1335	48	53	3	5	2	16	-9
43	1329	1328	45	105	-26	-61	-33	-57	-153
42	1310	1305	35	11	-15	-29	-34	-56	-11
41	1270	1264	59	123	20	27	11	17	156
40	1249	1248	5	4	8	8	-7	-11	
39*	1223	1220	119	113	-31	128	127	208	-45
38*	1210	1215	105	46	31	14	-28	-113	392
37	1204	1204	95	155	42	71	37	100	-35
36	1182	1181	84	74	-7	-114	-66	-98	-98
35	1163	1165	44	85	13	32	24	49	-54
34	1123	1125	169	154	-59	-140	-61	-170	-367
33	1103	1100	75	121	50	118	168	286	380
32	1082	1084	95	127	19	-15	-27	-69	
31	1057	1062	54	52	29	103	67	110	148
30	1039	1042	39	41	20	8	-16	-12	-93
29	1033	1032	54	46	-6	-43	-2	17	
28	1012	1014	172	176	-89	-190	-183	-311	-232
27	998	995	16	17	42	146	129	249	357
26	952	959	168	65	39	105	101	164	129
25	949	952	10	173	-17	-59	-43	-64	-75
24	931	939	11	13	8	26	9	13	31
23	919	927	34	108	-27	-30	26	54	-66
22	898	905	30	35	-21	-98	-103	-167	-127
21	878	886	121	269	14	-1	-59	-105	-106
20	831	842	31	15	1	-47	-129	-223	-118
19	807	821R	11		-12	-39	-29	-56	-32
18	790	788R	474		-4	22	9	1	
17	761	772R	139		-36	-53	62	116	
16	656	666R	2		-2	-5	-2	-3	
15	609	619R	28		29	73	113	193	
14	558	563R	59		-13	-23	-114	-196	
13	475	480R	47		16	52	76	128	
12	454	462R	22		-1	21	11	21	
11	416	442R	74		4	7	-46	-81	
10	386	394R	30		2	-19	13	20	
9	380	384R	8		-8	-30	88	167	
8	322	332R	157		21	-21	240	434	
7	297	302R	118		23	96	-93	-158	
6	255		13		-11	-17	-46	-77	
5	223		25		-11	-34	-12	-27	
4	198		49		2	6	-10	-22	
3	189		14		-1	7	4	10	
2	181		7		-7	-15	-16	-30	
1	126		223		13	10	-79	-143	
a					0.15	0.38	0.33	0.62	
δ					18	47	50	81	

FIG. 1. (1R)-(+)-Camphor (a) and (1S)-(-)- α -pinene (b).

EXC calculation gave results closer to the experiment than MFP/SCF for 9 transitions, and SUPER for 8. However, there is substantial uncertainty in the error of the measured values, and the poor performance of all theories for the peaks with experimental frequencies 1165, 1103 and 1130 cm^{-1} suggests that the normal modes may be misassigned. The experimental values are also quite dependent on molecular environment, as measured in Ref. 31.

In Table V analogous results are given for oxirane. Here, the larger AUG-cc-pVTZ basis was used for the EXC calculation, approximating the excitation energies with the KS MO energies. For the SUPER calculation, the 6-311G** basis was used and the excitation energies were recalculated for spin adapted singly excited Slater determinants. The B3LYP theory and the 6-311G** force field was used for both cases. Apparently, the GIAO calculation is superior to EXC for most of the modes. Nevertheless, except the C-H stretching modes where the harmonic approximation is not adequate, the results from MFP/GIAO and EXC are quite comparable. The SUPER approximation gave unreliable results for this molecule, as expected, although the calculated rotational strengths do more or less follow the experimental intensity pattern. The apparent poor performance of EXC in the C-H stretching region, indicated both for the α -pinane and oxirane molecules, can be perhaps explained by the character of the modes, where mainly translations of hydrogen atoms are involved. The EXC tensors are not translationally invariant

FIG. 2. VCD spectra of α -pinene. From top to bottom: simulated VCT, MFP and EXC spectra (B3LYP/6-31G** force field, HF/631G AAT), experimental spectrum in CCl_4 . Calculated spectra are magnified as indicated.

and the implementation of the Hellmann-Feynman theorem may be too crude for this type of motion. This could be improved if more realistic states and energies are used in formula (7) in this study, which would, obviously, make the whole method computationally more expensive. Recent works suggest, however, that accurate excitation energies can be obtained from the DFT approach as an alternative to the usual post-HF CI expansions.³³

As follows from the nature of the SOS methods (VCT, EXC), gauge independent atomic orbitals cannot be used here to remove the origin-dependence of the results. In our opinion, however, the universal distributed origin gauge is equivalent to the GIAO method for practical computations of VCD intensities. This is not true for NMR shielding, for example, where the magnetic perturbation cannot be localized.

VI. CONCLUSIONS

The excitation scheme in a combination with the hybrid HF-DFT calculations can be used as a faster alternative to

TABLE IV. Experimental and calculated rotatory strengths for propylene oxide. R_{EXC} and R_{SUPER} calculated at the Becke3LYP/6-31G** level, HF excitation energies used. Rotatory strengths in 10^{-9} Debye², ω in cm^{-1} .

ω_{EXP}^a	ω_{CAL}	R_{MFP}^a	R_{EXC}	R_{SUPER}	$R_{\text{EXP}}^a/\text{in } \text{CCl}_4$	in CS_2	Neat
1500	1548	-65	-74	-36	-40		-52
1456	1512	-02	57	22			
1444	1498	-12	-9	-77			
1406	1454	-125	-62	-307	-84		-208
1396	1416	-20	-37	-154	-33		-89
1264	1300	62	216	105		156	175
1165	1193	72	51	196	-4	4	-53
1143	1167	11	136	229	214	330	478
1130	1156	110	43	71	-159	-276	-406
1103	1134	8	-47	-299	81	145	152
1022	1042	-16	-62	100	-67	-66	-112
951	982	142	214	878	719	652	908
893	909	-263	-335	-622	-428	-331	-543
829	855	38	-285	-248			
748	781	-57	-247	-32		-216	-282

^aReference 31, MFP calculated with HF scaled force field, 6-31G** basis.

TABLE V. Experimental and calculated rotatory strengths for oxirane. R_{EXC} and R_{SUPER} calculated with the B3LYP force field, R_{EXC} with 6-311G** basis set for force field and AUG-cc-pVTZ basis for AAT, R_{SUPER} with 6-311G** basis. Units same as in Table IV.

$\omega_{\text{EXP}}^{\text{a}}$	ω_{CAL}	$R_{\text{GIAO}}^{\text{a,b}}$	R_{EXC}	R_{SUPER}	$R_{\text{EXP}}^{\text{a,c}}$
3028	3124	380	26	-580	114
3015	3119	-279	200	660	-89
2254	2299	145	-45	-5	121
2240	2286	-183	-79	7	-104
1397	1431	-86	-303	-750	-150g
1339	1364	-12	28	68	-25g
1235	1260	119	323	682	241
1112	1128	-19	-30	-34	-49
1106	1112	97	380	558	111
961	976	-276	-337	-24	-290
914	922	-42	-67	77	-62
885	895	69	-29	-21	50g
817	840	28	18	4	+g
754	754	101	74	-29	
673	664	-1	-2	22	

^aReference 32.

^bB3LYP/VD3P calculation.

^cGas-phase data marked by g, CCl₄ solution for C-H(D) modes, CS₂ solution otherwise.

the commonly used MFP and VCT methods for VCD spectra simulation. For α -pinene and propylene oxide the EXC procedure gave better agreement with the experiment than the VCT and MFP theories in the mid IR region. The results indicate that the scheme performs poorly for the C-H stretching modes and the current implementation is not suitable for benchmark calculations where the rotational and translational invariance of the tensors is required.

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