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Theoretical Prediction of the Optical Rotation of Chiral Molecules in Ordered Media: A Computational Study of (R_a)-1,3-Dimethylallene, (2R)-2-Methyloxirane, and (2R)-N-Methyloxaziridine

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A theoretical procedure has been developed and implemented to calculate the optical rotation of chiral molecules in ordered phase via origin-independent diagonal components $\kappa'_{xx}(-\omega;\omega)$, $\kappa'_{yy}(-\omega;\omega)$, $\kappa'_{zz}(-\omega;\omega)$ of the optical activity tensor and origin-independent components $A_{\alpha,\beta\gamma}(-\omega;\omega)$, for $\alpha \neq \beta \neq \gamma$, of the mixed electric dipole-electric quadrupole polarizability. Origin independence was achieved by referring these tensors to the principal axis system of the electric dipole dynamic polarizability $\alpha_{\alpha\beta}(-\omega;\omega)$ at the same laser frequency ω. The approach has been applied, allowing for alternative quantum mechanical methods based on different gauges, to estimate near Hartree–Fock values for three chiral molecules, (2R)-N-methyloxaziridine C_2NOH_5, (2R)-2-methyloxirane (also referred to as propylene oxide) C_3OH_6, and (R_a)-1,3-dimethylallene C_5H_8, at two frequencies. The theoretical predictions can be useful for an attempt at measuring correspondent experimental values in crystal phase. © 2015 Wiley Periodicals, Inc.

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Introduction

Although a wealth of information on the natural optical activity of molecules in disordered phase is available,[1–3] chiroptical properties of crystals have comparatively received less attention from the theoretical and computational points of view. An expression for the optical rotation per unit path length of molecules in an anisotropic medium has been obtained by Buckingham and Dunn within the framework of time-dependent perturbation theory.[4] A band theory was proposed by Natori[5] but to the best of our knowledge, has not been used in *ab initio* calculations. Computations of natural optical activity in solids at optical wavelengths have been reported by Zhong et al.[6–8] A comprehensive review discussing experimental and phenomenological distinctive features of circular birefringence and related properties in nonabsorbing crystals was published by Kaminsky.[9] A band theory of spatial dispersion in magnetoelectrics by Malashevich and Souza[10] appeared more recently.

The plane of a polarized plane wave is rotated by freely-tumbling chiral molecules in disordered media, that is, in solution or gas phase. The angle ϕ of rotation per unit path length is rationalized via the trace $\kappa'_{\alpha\alpha}$ of a "mixed electric-magnetic dipole polarizability" (MEMDP) second-rank tensor $\kappa'_{\alpha\beta}$.[3,4,11–22] The pseudoscalar $\kappa'_{\alpha\alpha}$, even under time reversal T and odd under parity P, is invariant in a translation of reference frame. Accordingly, it has long been considered the only measurable part of the MEMDP tensor. This feature constitutes a drawback, because $\kappa'_{\alpha\alpha}$ is quite small, as the three (usually much larger) diagonal components, κ'_{xx}, κ'_{yy} and κ'_{zz}, have different sign, in general. Regrettably, the individual components of MEMDP, diagonal and off-diagonal, depend on the origin,[23–25] and,

therefore, they could not, in principle, be univocally determined in an ordered medium, for example, a molecular crystal.

In oriented molecules, ϕ has been shown to depend also on $A_{\alpha,\beta\gamma}$, the mixed electric dipole-electric quadrupole polarizability (MEDQP),[15] via an origin-independent combination of terms which separately depend on the origin.[3,4] At a given frequency ω of the incident monochromatic light, the change of the individual $\kappa'_{\alpha\beta}(-\omega;\omega)$ and $A_{\alpha,\beta\gamma}(-\omega;\omega)$ components in a translation of the origin is described by equations involving the dynamic electric dipole polarizability (EDP), $\alpha_{\alpha\beta}(-\omega;\omega)$, at the same frequency.[4,18,19,26,27] However, it was recently observed that the diagonal components of the MEMDP tensor become translationally invariant if it is referred to the coordinate frame of the eigenvectors of EDP.[28] As shown in this article, this is also the case of the $A_{\alpha,\beta\gamma}$ components for $\alpha \neq \beta \neq \gamma$.

In a previous work,[28] the theory had been applied, at the random-phase approximation (RPA)[29] level, to 1,2-M-dioxin, $C_4H_4O_2$, an unstable molecule not isolated so far, to determine origin-independent diagonal components of $\kappa'_{\alpha\beta}(-\omega;\omega)$. The results arrived at in that paper constituted a computational check of the algorithm implemented in the SYSMO code.[30]

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Three stable chiral molecules have been taken into account in this study, (2R)-N-methyloxaziridine C_2NOH_5, (2R)-2-methyl-oxirane C_3OH_6, and (R_a)-1,3-dimethylallene C_5H_8. This choice was motivated by the medium size of these compounds, which makes near Hartree–Fock (HF) accuracy achievable, by their intrinsic interest as candidates for chiral discrimination via nuclear magnetic resonance spectroscopy,[31,32] and by the attention paid in previous investigations. The specific rotation[33] of C_3OH_6 at 355 nm has been measured.[34] Theoretical predictions have been reported later on for this compound[35–37] and for C_5H_8.[35]

This article sets out to report translationally invariant components κ'_{xx}, κ'_{yy} and κ'_{zz} of MEMDP and $A_{\alpha,\beta\gamma}$ for $\alpha \neq \beta \neq \gamma$ of MEDQP, which are possibly measurable. The optical rotation per unit path length and the specific rotation in ordered phase have also been evaluated. The theoretical scheme is outlined in Theoretical method section and an account of the calculations is given in Calculations section. Concluding remarks are reported in Concluding remarks and outlook section.

Theoretical Method

Equation (22) from the paper by Buckingham and Dunn.[4] can be recast in the form

$$\phi = -\frac{1}{2}\omega\mu_0\mathcal{N}\zeta'_{xyz},\qquad(1)$$

with

$$\zeta'_{xyz} = \kappa'_{\alpha\alpha} - \kappa'_{zz} + \frac{1}{3}\omega(A_{x,yz} - A_{y,xz})\qquad(2)$$

for a beam of light of angular frequency ω propagating in the z direction through an anisotropic medium. In these relationships, μ_0 is the permeability of a vacuum, $\mathcal{N}$ is the number density,

$$\kappa'_{\alpha\beta}(-\omega;\omega) = -\frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega}{\omega_{ja}^2-\omega^2}\Im(\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{m}_\beta|a\rangle)\qquad(3)$$

is the MEMDP tensor[28] and

$$A_{\alpha,\beta\gamma}(-\omega;\omega) = \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\Re(\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\Theta}_{\beta\gamma}|a\rangle)\qquad(4)$$

is the MEDQP tensor. The Einstein convention of summing over repeated Greek indices is used throughout this article. The electronic operators are denoted as in previous papers,[28] for example, the electric dipole moment is

$$\hat{\mu}_\alpha = -e\sum_{i=1}^n r_{i\alpha},$$

the magnetic dipole moment is

$$\hat{m}_\alpha = -\frac{e}{2m_e}\sum_{i=1}^n \hat{l}_{i\alpha},$$

and the traceless quadrupole moment operator is defined as

$$\hat{\Theta}_{\alpha\beta} = -\frac{1}{2}e\sum_{i=1}^n (3r_\alpha r_\beta - r^2\delta_{\alpha\beta})_i.$$

In a translation of the coordinate frame

$$\boldsymbol{r}'' = \boldsymbol{r}' + \boldsymbol{d},\qquad(5)$$

one finds for the different origins,[15,18]

$$\kappa'_{\alpha\beta}(\boldsymbol{r}'') = \kappa'_{\alpha\beta}(\boldsymbol{r}') - \frac{\omega}{2}\epsilon_{\beta\gamma\delta}\alpha_{\alpha\gamma}d_\delta,\qquad(6)$$

with

$$\kappa'_{\alpha\alpha}(\boldsymbol{r}'') = \kappa'_{\alpha\alpha}(\boldsymbol{r}') \equiv \mathrm{Tr}[\boldsymbol{\kappa}']\qquad(7)$$

and

$$A_{\alpha,\beta\gamma}(\boldsymbol{r}'') = A_{\alpha,\beta\gamma}(\boldsymbol{r}') - \frac{3}{2}d_\beta\alpha_{\alpha\gamma} - \frac{3}{2}d_\gamma\alpha_{\alpha\beta} + d_\delta\alpha_{\alpha\delta}\delta_{\beta\gamma}.\qquad(8)$$

According to Eqs. (6)–(8), the quantity

$$I_{xyz} = \frac{1}{3}\omega(A_{x,yz} - A_{y,xz}) - \kappa'_{zz}\qquad(9)$$

is invariant of the origin of an arbitrary coordinate system.[3,4] However, the individual terms appearing in Eq. (9) can be made separately invariant of the origin by a judicious choice of reference frame. In fact, the diagonal components $\kappa'_{xx}(-\omega;\omega)$, $\kappa'_{yy}(-\omega;\omega)$ and $\kappa'_{zz}(-\omega;\omega)$ of MEMDP, and $A_{x,yz}(-\omega;\omega)$ and $A_{y,xz}(-\omega;\omega)$ of MEDQP are origin independent, according to Eqs. (6) and (8), respectively, if these tensors are referred to the principal axis system of the dynamic EDP,

$$\alpha_{\alpha\beta}(-\omega;\omega) = \frac{1}{\hbar}\sum_{j\neq a}\frac{2\omega_{ja}}{\omega_{ja}^2-\omega^2}\Re(\langle a|\hat{\mu}_\alpha|j\rangle\langle j|\hat{\mu}_\beta|a\rangle).\qquad(10)$$

Thus, it seems convenient to adopt such a reference frame to univocally define measurable components of tensors (3) and (4).

The Eqs. (6), (7), and (9) are exactly fulfilled if the molecular properties have been determined via exact eigenfunctions to a model Hamiltonian, for example, for the true HF states, or by optimal variational wavefunctions.[38] Therefore, in a calculation of MEMDP and MEDQP tensors relying on the algebraic approximation, Eqs. (6), (7), and (9) are satisfied only in the limit of a complete basis set. Nonetheless, a proper choice of gauge can enable one to fulfill these equations exactly, irrespective of the quality of a given basis set. The basic hint is provided by the equation for the change of MEMDP either within the dipole velocity-angular momentum (P, L) picture,

$$\kappa'^{(P,L)}_{\alpha\beta}(-\omega;\omega)=-\frac{e^2}{2m_e^2\hbar}\sum_{j=a}\frac{2\omega}{\omega_{ja}\left(\omega_{ja}^2-\omega^2\right)}\Re\left(\langle a|\hat{P}_\alpha|j\rangle\langle j|\hat{L}_\beta|a\rangle\right),$$
(11)

or dipole acceleration-torque (F, K) picture,[19,26,28]

$$\kappa'^{(F,K)}_{\alpha\beta}(-\omega;\omega)=-\frac{e^2}{2m_e^2\hbar}\sum_{j=a}\frac{2\omega}{\omega_{ja}^3\left(\omega_{ja}^2-\omega^2\right)}\Re\left(\langle a|\hat{F}^N_{n\alpha}|j\rangle\langle j|\hat{K}^N_{n\beta}|a\rangle\right).$$
(12)

For the MEMDP tensor[28]

$$\kappa'^{(P,L)}_{\alpha\beta}(\mathbf{r}'')=\kappa'^{(P,L)}_{\alpha\beta}(\mathbf{r}')-\frac{\omega}{2}\epsilon_{\beta\gamma\delta}\alpha^{(P,P)}_{\alpha\gamma}d_\delta,$$
(13)

$$\kappa'^{(F,K)}_{\alpha\beta}(\mathbf{r}'')=\kappa'^{(F,K)}_{\alpha\beta}(\mathbf{r}')-\frac{\omega}{2}\epsilon_{\beta\gamma\delta}\alpha^{(F,F)}_{\alpha\gamma}d_\delta,$$
(14)

where the EDP $\alpha_{\alpha\beta}\equiv\alpha^{(R,R)}_{\alpha\beta}$, defined via Eq. (10) within the (R, R) dipole length gauge, is instead represented either in the velocity or acceleration gauges,[28]

$$\alpha^{(P,P)}_{\alpha\beta}(-\omega;\omega)=\frac{e^2}{m_e^2\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}\left(\omega_{ja}^2-\omega^2\right)}\Re\left(\langle a|\hat{P}_\alpha|j\rangle\langle j|\hat{P}_\beta|a\rangle\right),$$
(15)

$$\alpha^{(F,F)}_{\alpha\beta}(-\omega;\omega)=\frac{e^2}{m_e^2\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}^3\left(\omega_{ja}^2-\omega^2\right)}\Re\left(\langle a|\hat{F}^N_{n\alpha}|j\rangle\langle j|\hat{F}^N_{n\beta}|a\rangle\right).$$
(16)

Within the principal axes system of $\alpha^{(P,P)}_{\alpha\beta}$, $\kappa'^{(P,L)}_{xx}$, $\kappa'^{(P,L)}_{yy}$ and $\kappa'^{(P,L)}_{zz}$ will stay the same, according to Eq. (13). Similarly, within the principal axis system of $\alpha^{(F,F)}_{\alpha\beta}$, $\kappa'^{(F,K)}_{xx}$, $\kappa'^{(F,K)}_{yy}$ and $\kappa'^{(F,K)}_{zz}$ will be invariant on account of Eq. (14). Analogously, the $A_{x,yz}$ and $A_{y,xz}$ components are invariant if referred to the principal axis system of the $\alpha^{(R,R)}_{\alpha\beta}$ EDP in the dipole length (R, R) gauge. One is referred to Ref. [28] for a detailed explanation of the symbols and tensor notation.

A theoretical prediction of translationally invariant diagonal components of κ' is obtained via the approaches outlined here using the following procedure,

- For a given frequency ω, the 3×3 eigenvalue equation for the dynamic EDP, for example, in the (P, P) picture, Eq. (15),

$$\boldsymbol{\alpha}^{(P,P)}\mathbf{U}=\mathbf{U}\boldsymbol{\lambda}^{(\alpha)},$$
(17)

  is solved, determining the eigenvalues $\boldsymbol{\lambda}^{(\alpha)}$ and the eigenvectors $\mathbf{U}$,
- the similarity transformation

$$\boldsymbol{\kappa}'^{(P,L)}_D=\mathbf{U}^\dagger\boldsymbol{\kappa}'^{(P,L)}\mathbf{U}$$
(18)

  of MEMDP within the (P, L) gauge, Eq. (11), is performed, to obtain the representation $\boldsymbol{\kappa}'^{(P,L)}_D$ of the MEMDP tensor in the principal axis system defined by the eigenvectors $\mathbf{U}$,
- the new coordinates of the Ith nucleus become

$$\mathbf{R}_{I,D}=\mathbf{U}\mathbf{R}_I.$$
(19)

The diagonal components of the $\boldsymbol{\kappa}'^{(P,L)}_D$ tensor, referred to the principal axis system of $\boldsymbol{\alpha}^{(P,P)}$, are origin independent accord-

ing to Eq. (13). A similar procedure can be defined within the dipole acceleration/torque formalism, using $\boldsymbol{\kappa}'^{(F,K)}$, Eq. (12), $\boldsymbol{\alpha}^{(F,F)}$, Eq. (16), and relationships analogous to Eqs. (17)–(18). Origin-independent $A_{x,yz}$ and $A_{y,xz}$ components are similarly obtained by a trasformation to the principal axis system of $\boldsymbol{\alpha}^{(R,R)}$,

$$A_{\alpha,\beta\gamma}=A_{\alpha',\beta'\gamma'}U_{\alpha'\alpha}U_{\beta'\beta}U_{\gamma'\gamma}.$$
(20)

The eigenvectors $\mathbf{U}$ of $\boldsymbol{\alpha}^{(R,R)}$ are obtained by a relationship analogous to Eq. (17). Of course they would coincide with those of $\boldsymbol{\alpha}^{(P,P)}$ and $\boldsymbol{\alpha}^{(F,F)}$ in the ideal case of complete basis set.

A priori there is no preferential gauge for the calculation of EDPs and MEMDPs.[28] In practice, however, the dipole velocity/angular momentum (P, L) gauge is sometimes preferable for computing $\kappa'^{(P,L)}_D$. In fact, in a calculation allowing for the algebraic approximation to construct the electronic wavefunction of a molecule, this choice is favored compared to $\kappa'^{(F,K)}_D$, due to problems concerning the representation of the force and torque operators via, for instance, Gaussian basis sets.[28]

One can add that, if a series of sum rules based on off-diagonal hypervirial relationships[38] are satisfied, for instance, in the case of exact or optimal variational electronic wavefunctions, or complete basis sets, both the procedures using either $\boldsymbol{\alpha}^{(P,P)}$ or $\boldsymbol{\alpha}^{(F,F)}$ would provide the same numerical response, that is, the invariant diagonal components of $\kappa'^{(P,L)}_D$ and $\kappa'^{(F,K)}_D$ would coincide. For instance, within the *true* coupled Hartree–Fock approach,[38] equivalent to RPA[29] used in this study, results arrived at via alternative computational recipes (11) and (12), as well as (15) and (16), would be identical. In actual self-consistent field (SCF) calculations adopting truncated basis sets, the closeness of the values obtained in different pictures will give a measure of basis set completeness, ability to represent a given operator in different gauges, and eventually, of accuracy.

In most recent calculations of $\kappa'_{\alpha\alpha}$, London atomic orbitals (LAO),[39] also referred to as gauge including atomic orbitals,[40] (This is the first reference in which the reinterpretation of the GIAO acronym for gauge-including-atomic-orbitals has been proposed, see footnote 6, p. 5047.) have been used[20–22] to ensure its origin independence. At any rate, the individual components, diagonal and off-diagonal, of the MEMDP tensor computed via a LAO basis set are origin dependent.[22] Moreover, the intrinsic origin dependence of the $A_{\alpha,\beta\gamma}$ MEDQP tensor, with $\alpha \neq \beta \neq \gamma$, cannot be overcome, unless it is referred to the principal axis system of $\boldsymbol{\alpha}^{(R,R)}$.

There is an additional problem related to the use of LAO's within coupled cluster (CC) perturbation theory. At variance with the HF, multiconfigurational self consistent field and density functional theory approaches, the inclusion of London orbitals does not remove the problem of origin dependence in CC calculations.[41,42] A solution has been suggested by Pedersen et al.[43]

Calculations

The theoretical procedure outlined above has been applied to calculate origin-independent components of MEMPD and MEDQP tensors in (2*R*)-2-methyloxirane, (*R*ₐ)-1,3-dimethylallene
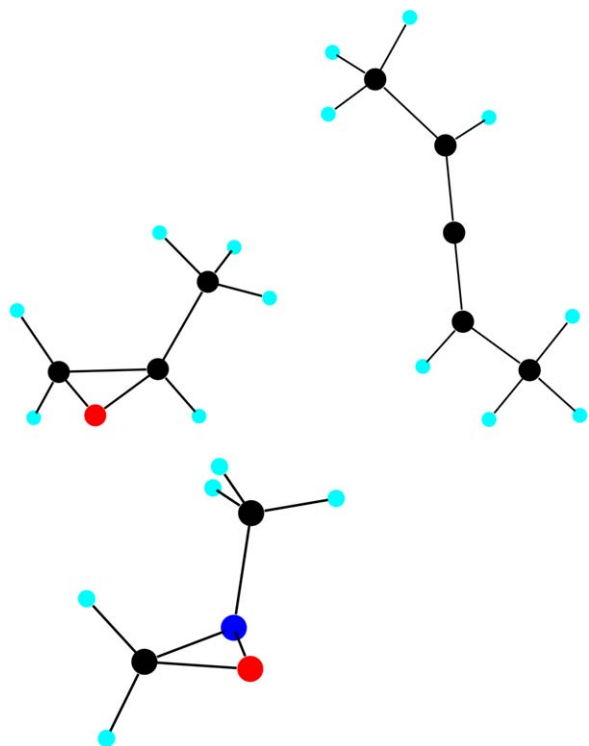
Figure 1. From top-left, in clockwise direction, $(2R)$-2-Methyloxirane C_3OH_6, (R_a)-1,3-Dimethylallene C_5H_8 and $(2R)$-N-Methyloxaziridine C_2NOH_5 molecules.
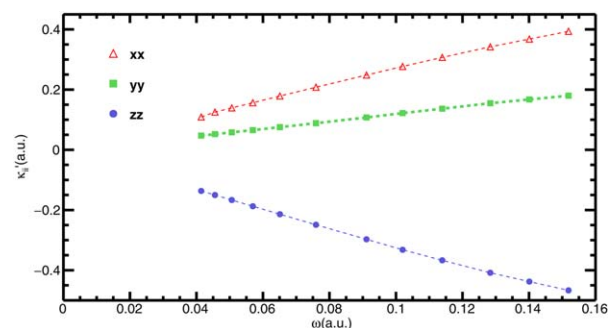

Figure 2. The diagonal components of the $\kappa'^{(P,L)}$ tensor of (R_a)−1,3-dime-thylallene in the principal axes system of $\alpha^{(P,P)}$ versus the frequency.

frames and to apply Eqs. (17), (18), and (20). As shown in the Supporting Information available, these eigenvectors are virtually identical to three significant figures.

Analogously, MEMDP's have been computed in six formalisms, using angular momentum and torque representations for the electronic interaction with the magnetic field of the impinging radiation. Values of the diagonal components of the $\kappa'^{(P,L)}$ computed for (R_a)-1,3-dimethylallene in the principal axes system of $\alpha^{(P,P)}$ are displayed in Figure 2 as a function of the frequency ω. The difference $\Delta A = A_{x,yz} - A_{y,xz}$ of (R_a)-1,3-dimethylallene in the principal axes system of $\alpha^{(R,R)}$ versus ω is shown in Figure 3.

Detailed supporting information on these calculations, needed to reproduce the results obtained, is reported. The overall agreement among predictions from length, velocity, and acceleration pictures gives a benchmark of high accuracy of the present calculations. The numerical information displayed in Table 2 for MEMDP within (R, L), (P, L), and (F, K) representations documents the practicality of the approach discussed earlier. The results are very close to one another, as expected from the virtual completeness of the extended basis sets used.

Accordingly, one can reasonably expect that also the predictions for MEDQP reported in Table 3 are of near HF quality.

and $(2R)$-N-Methyloxaziridine, see Figure 1, at the SCF-RPA level of accuracy via the SYSMO package.[30] The molecular geometry and the large basis sets for C, O, N, and H atoms are the same as those used in a previous study.[31] Near HF quality of the predictions has been established by comparing EDP's calculated within six different formalisms, allowing for dipole length, velocity and acceleration gauges.[28] The values displayed in Table 1 for two frequencies, within the (R, R), (P, P), and (F, F) representations, have been used to determine the corresponding eigenvector

Table 1. EDP tensors of (R_a)−1,3-dimethylallene, $(2R)$−2-methyloxirane and $(2R)$-N-methyloxaziridine within the (R, R), (P, P), and (F, F) gauges in the corresponding principal axes systems, in a.u.[a]

Molecule	Comp.	$\omega = 0.0345439$ a.u.			$\omega = 0.0773571$ a.u.		
		(R, R)	(P, P)	(F, F)	(R, R)	(P, P)	(F, F)
C_2NOH_5	xx	43.076	43.038	42.937	43.819	43.781	43.679
	yy	34.408	34.354	34.299	34.894	34.840	34.785
	zz	31.875	31.843	31.760	32.336	32.304	32.219
	av	36.453	36.412	36.332	37.017	36.975	36.894
C_3OH_6	xx	45.189	45.150	45.065	45.967	45.927	45.841
	yy	35.295	35.260	35.168	35.780	35.745	35.651
	zz	36.282	36.252	36.172	36.798	36.769	36.687
	av	38.922	38.887	38.802	39.515	39.480	39.393
C_5H_8	xx	50.170	50.116	50.049	51.035	50.981	50.911
	yy	101.64	101.59	101.54	106.07	106.02	105.97
	zz	50.560	50.506	50.440	51.426	51.370	51.303
	av	67.457	67.405	67.343	69.511	69.458	69.396

[a] The conversion factor to SI units is 1 a.u. of EDP $e^2 a_0^2/E_h = 1.648\ 777\ 2536 \times 10^{-41}$ C^2 m^2 $J^{-1} \equiv Fm^2$. The conversion factor of the angular frequency is 1 a.u. of $\omega = E_h/\hbar = 4.134\ 137\ 335 \times 10^{16}$ rad s^{-1} from CODATA Recommended Values of the Fundamental Physical Constants.[44] The wavelength expressed in meters is obtained from $\lambda = 2\pi c/\omega = 4.556\ 335\ 25 \times 10^{-8}/\omega$ for ω in a.u. Therefore, the frequencies 0.03454339 and 0.0773571 a.u. correspond to 1319 and 589 nm, respectively.
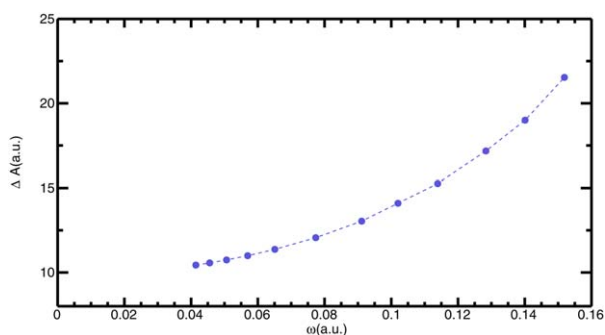
Figure 3. $\Delta A = A_{x,yz} - A_{y,xz}$ of (R_a)-1,3-dimethylallene in the principal axes system of $\boldsymbol{\alpha}^{(R,R)}$ as a function of the frequency.

Therefore, the rotation angles per unit path length and 1 amagat of number density, for two different frequencies, displayed in Table 4 can provide useful indications for experimental determinations. For the magnetic constant (permeability of vacuum), we used the value $\mu_0 = 6.691762496807159 \times 10^{-4}$ a.u. $(a_0 m_e\ e^{-2})$, corresponding to $4\pi \times 10^{-7}$ NA^{-2}, from CODATA.[44] For the number density $\mathcal{N}$, we used 1 amagat = $2.6867774 \times 10^{-25}$ m^{-3} as a practical unit referred to an ideal gas at 273.15 K and 1 atm (101.325 kPa). This yardstick, corresponds to $3.98139 \cdot 10^{-6} a_0^{-3}$ a.u.[45]

The specific rotation[33] of plane polarized light of wavelength λ in units of degrees [dm(g/cm^3)]$^{-1}$ is calculated via[30,35,36,46]

$$[\alpha]_\lambda = 1.34229 \times 10^{-4} \beta \bar{v}^2 (n^2 + 2)/3M \qquad (21)$$

$$\beta = -\frac{1}{3\omega} Tr[\boldsymbol{\kappa}'(-\omega; \omega)] \qquad (22)$$

where β is the optical rotation parameter, in units of (bohr)^4, $\bar{v}$ is the radiation wavenumber in cm^{-1}, the Lorentz factor $(n^2 + 2)/3$ is defined via the refractive index n of the medium, and M is the molar mass in g/mol. Values of $[\alpha]_\lambda$ computed within the (P, L) and (F, K) gauges are invariant of the origin. The results of the calculation are displayed in Table 5. They are quite close to one another for the three formalisms, which is a further indication of near HF quality of the theoretical estimates.

The computed $[\alpha]_\lambda$ value at the sodium D line for dimethylallene in Table 5 is very close to the HF estimate of Giorgio et al.[36] but that for methyloxirane is approximately two times bigger. The prediction of the correct sign and magnitude of the specific rotation of methyloxirane at the experimental wavelength of 355 nm via theoretical calculations revealed a very difficult task.[35,47,48] The experimental value[34] for (S)-propylene oxide, or (S)-methyloxirane, is $[\alpha]_\lambda = 10.2 \pm 2.9$ deg dm^{-1} (g/cm^3)$^{-1}$ for $\lambda = 355$ nm, corresponding to $\omega = 0.12835$ a.u. Thus, the sign of computed $[\alpha]_\lambda$ values for $\lambda = 355$ nm, reported in Table 5 for the (R) enantiomer of 2-methyloxirane, is the *opposite*. DFT/B3LYP calculations provided a positive optical rotation for the S enantiomer at 355 nm, in agreement with experiment.[35,47] However, Tam et al.[47] argue that this result is a consequence of the incorrect prediction by the

Table 2. MEMDP tensors of (R_a)-1,3-dimethylallene, (2R)-2-methyloxirane and (2R)-N-methyloxaziridine within the (R, L), (P, L), and (F, K) representations, in the corresponding principal axes systems of the (R, R), (P, P), and (F, F) dipole polarizabilities, in a.u.[a]

Molecule	Comp.	$\omega = 0.0345439$ a.u			$\omega = 0.0773571$ a.u.		
		(R, L)	(P, L)	(F, K)	(R, L)	(P, L)	(F, K)
C$_2$NOH$_5$	xx	−0.10302	−0.10303	−0.10192	−0.23981	−0.23981	−0.23720
	yy	0.02652	0.02655	0.02650	0.06156	0.06163	0.06147
	zz	0.05512	0.05517	0.05483	0.12676	0.12687	0.12608
	xy	0.14113	0.14114	0.14064	0.33021	0.33023	0.32910
	yx	−0.03519	−0.03461	−0.03724	−0.08755	−0.08618	−0.09254
	xz	−0.09503	−0.09541	−0.09551	−0.21314	−0.21406	−0.21426
	zx	0.17296	0.17260	0.17473	0.39301	0.39215	0.39729
	yz	0.20299	0.20293	0.20239	0.46758	0.46743	0.46618
	zy	−0.19719	−0.19682	−0.19666	−0.45128	−0.45041	−0.45011
	av	−0.00713	−0.00710	−0.00687	−0.01716	−0.01710	−0.01655
C$_3$OH$_6$	xx	−0.04306	−0.04342	−0.04317	−0.09795	−0.09877	−0.09821
	yy	0.00939	0.00950	0.00943	0.02209	0.02234	0.02218
	zz	0.03198	0.03209	0.03190	0.07242	0.07267	0.07224
	xy	0.01497	0.01394	0.01323	0.02661	0.02432	0.02272
	yx	−0.15160	−0.15006	−0.14956	−0.34117	−0.33771	−0.33662
	xz	0.19549	0.19571	0.19627	0.45082	0.45126	0.45254
	zx	−0.22998	−0.23035	−0.23201	−0.53117	−0.53189	−0.53570
	yz	0.18737	0.18734	0.18680	0.42775	0.42771	0.42651
	zy	−0.16119	−0.16096	−0.16071	−0.36714	−0.36659	−0.36603
	av	−0.00057	−0.00061	−0.00061	−0.00115	−0.00125	−0.00126
C$_5$H$_8$	xx	0.09507	0.09517	0.09546	0.21154	0.21175	0.21253
	yy	0.03943	0.03930	0.03873	0.09058	0.09029	0.08898
	zz	−0.11390	−0.11395	−0.11419	−0.25335	−0.25346	−0.25418
	xy	0.01400	0.01447	0.01447	0.01647	0.01766	0.01783
	yx	0.97543	0.97523	0.97336	2.34690	2.34638	2.34198
	av	0.00687	0.00684	0.00667	0.01626	0.01619	0.01578

[a] The conversion factor to SI units is 1 a.u. of MEMDP $e^2 a_0^3/\hbar = 3.607\ 015\ 64 \times 10^{-35}$ F m^3 s$^{-1} \equiv$ m kg^{-1} s C^2, from CODATA Recommended Values of the Fundamental Physical Constants.[44]

Table 3. MEDQP tensors of (R_a)-1,3-Dimethylallene, $(2R)$-2-Methyloxirane and $(2R)$-N-Methyloxaziridine, within the (R) representation, in the corresponding principal axes of the (R, R) EDP, in a.u.[a]

Molecule	Comp.	$\omega = 0.0345439$	$\omega = 0.0773571$
C_2NOH_5	x, xx	−29.147	−29.734
	x, yy	17.888	18.385
	x, zz	11.259	11.349
	x, xy	−21.635	−21.999
	x, xz	3.208	3.402
	x, yz	3.131	3.209
	y, xx	0.766	0.751
	y, yy	−3.400	−3.310
	y, zz	2.633	2.559
	y, xy	−9.934	−10.096
	y, xz	0.331	0.342
	y, yz	8.029	8.127
	z, xx	−15.501	−15.886
	z, yy	−3.326	−3.469
	z, zz	18.828	19.354
	z, xy	2.167	2.245
	z, xz	−11.261	−11.439
	z, yz	−20.691	−21.099
C_3OH_6	x, xx	−16.036	−16.065
	x, yy	6.905	6.778
	x, zz	9.131	9.287
	x, xy	27.441	28.245
	x, xz	−16.132	−16.112
	x, yz	2.966	3.050
	y, xx	2.146	2.127
	y, yy	8.427	8.440
	y, zz	−10.573	−10.567
	y, xy	−17.705	−18.184
	y, xz	1.410	1.422
	y, yz	−3.404	−3.432
	z, xx	4.053	4.187
	z, yy	17.875	17.882
	z, zz	−21.928	−22.069
	z, xy	2.322	2.352
	z, xz	−11.222	−11.282
	z, yz	17.600	18.484
C_5H_8	x, xz	−5.862	−5.886
	x, yz	−6.365	−6.333
	y, xz	−16.625	−18.402
	y, yz	−5.016	−4.425
	z, xx	8.596	8.459
	z, yy	−12.992	−13.458
	z, zz	4.396	4.999
	z, xy	−6.398	−6.389

[a] Symmetry unique nonvanishing components. The conversion factor to SI units is 1 a.u. of MEDQP $e^2 a_0^3/E_h = 8.724\,953\,447 \times 10^{-52}$ C^2 m^3 $J^{-1} \equiv$ F m^3, from CODATA Recommended Values of the Fundamental Physical Constants.[44]

Table 4. Optical rotation per unit path length within the (R, L) gauge, ϕ (rad m^{-1}).[a]

Molecule	ω	$\phi_{\kappa'}$	ϕ_A	ϕ	ϕ_{iso}
C_2NOH_5	0.0345439	0.0665	−0.0280	0.0385	0.0124
	0.0773571	0.3470	−0.1440	0.2031	0.0668
C_3OH_6	0.0345439	0.0293	−0.0156	0.0137	0.0010
	0.0773571	0.1477	−0.0817	0.0660	0.0045
C_5H_8	0.0345439	−0.1170	−0.1027	−0.2197	−0.0119
	0.0773571	−0.5883	−0.6060	−1.1944	−0.0633

[a] For $\mathcal{N} = 1$ amagat $\equiv 3.98139 \cdot 10^{-6} a_0^{-3}$ a.u., see Eq. (1), $\phi = \phi_{\kappa'} + \phi_A$ denotes the rotation angle per unit path length for a linearly polarized beam of light of angular frequency ω (in a.u.) propagating in the z direction through an anisotropic medium, $\phi_{\kappa'} = C\omega[\kappa'_{\alpha\alpha} - \kappa'_{zz}]$, $\phi_A = (1/3)C\omega^2[A_{x,yz} - A_{y,xz}]$, $\phi_{iso} = (2/3)C\omega\kappa'_{\alpha\alpha}$ is the rotation in isotropic phase. For $\kappa'_{\alpha\alpha}$ in a.u. from Table 2, $C = -\frac{1}{2}\mu_0\mathcal{N}/a_0 = -25.1735$.

Table 5. Specific rotation $[\alpha]_\lambda$, Eq. (21), in units of degrees $[dm(g/cm^3)]^{-1}$.[a]

Molecule	Picture	$\lambda = 1319$	$\lambda = 589$	$\lambda = 355$
C_2ONH_5	(R, L)	27.0	145	477
	(P, L)	26.9	145	476
	(F, K)	26.0	140	462
C_3OH_6	(R, L)	2.18	9.90	18.2[b]
	(P, L)	2.35	10.8	20.9
	(F, K)	2.37	10.9	21.2
C_5H_8	(R, L)	−22.5	−119	−362
	(P, L)	−22.4	−119	−361
	(F, K)	−21.9	−116	−351

[a] Calculated within the (R, L), (P, L), and (F, K) pictures. Wavelengths λ in nm. Values of $[\alpha]_\lambda$ are not corrected for the Lorentz factor $(n^2+2)/3$. [b] The experimental $[\alpha]_\lambda$ is -10.2 ± 2.9.[34]

(SAOP) functional are reported. The SAOP functional gives the correct lowest Rydberg excitation, which results in significant overestimation of the optical rotation.

Concluding Remarks and Outlook

The theoretical predictions reported for sharply defined tensor components κ'_{xx}, κ'_{yy}, κ'_{zz}, $A_{\alpha,\beta\gamma}$ for $\alpha \neq \beta \neq \gamma$, and optical rotations ϕ provide reliable estimates of corresponding measurable values. Allowing for the calculations performed for these molecules, corresponding experimental information could be obtained by measurements in ordered media.

To determine the experimental diagonal components of the $\boldsymbol{\kappa}'$ tensor, differential Rayleigh scattering of left- and right-circularly polarized light, can be used, see Buckingham and Dunn,[4] Kaminsky,[9] and references therein. Actually, nematic liquid crystal solvents, effectively used to study the extent to which molecular orientation bias nuclear magnetic resonance spectral parameters, may be unsuitable for chiral species, as optically active solutes convert nematic mesophases into the cholesteric form.[50] The experimental electric polarizabilities at the same frequency can be obtained by well-known techniques. Average values are measurable from the refractive index of a low-pressure gas.[51,52] A combination of average values with light scattering data[50] gives the anisotropy and the

B3LYP functional of the energy for the excitation to the lowest Rydberg state. This remarkable contradiction between theory and experiment has been discussed by Ruud and Zanasi.[37] According to these authors, the sign change of the optical rotation of methyloxirane should be imputed to effects arising from molecular vibration.

As regards the discussion of the optical rotation of methyl oxirane at 355 nm, it was shown by Kongsted et al.[49] that both vibrations (incl. temperature effects via Boltzmann averaging) and higher-order correlation effects contribute significantly to the optical rotation in gas phase. In the same paper, KS-DFT calculations with the statical averaged orbital-dependent potential

principal components of the frequency-dependent polarizability for molecules with a threefold or higher symmetry axis. The optical activity of uniaxial crystals or of oriented molecules can also be considered.[50]

Although, in principle, $\alpha_{\alpha\beta}(-\omega;\omega)$, $\kappa'_{\alpha\beta}(-\omega;\omega)$ and $A_{\alpha,\beta\gamma}$ should be experimentally determined, a viable procedure can be designed by merging calculation and experiment. Actually, the eigenvectors of the EDP, for any frequency ω, can be obtained to a high degree of accuracy via computational methods of quantum chemistry, so that experimental data are needed only for $\kappa'_{\alpha\beta}(-\omega;\omega)$ and $A_{\alpha,\beta\gamma}$. The latter could be separately available from depolarized collision-induced light scattering experiments.[53–55]

The diagonal components of the MEMDP tensor are, in general, one order of magnitude bigger than the averaged trace. Their experimental determination would constitute a major achievement, making chiral discrimination much easier. Analogously, according to the present calculations, the rotation per unit path length is one order of magnitude bigger than that observable in disordered media.

Eventually, reliable predictions of these quantities for crystals would require proper matching of the electronic crystal momentum with the photon momentum.[10] In future work, one should also attempt at verifying if the single-molecule calculations presented here are a reasonably accurate approximation to results computed using Wannier orbitals for the entire (infinite) crystal.

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