The far-infrared molecular dynamics of circular dichroism and optical rotatory dispersion

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The nature of the far-infrared molecular dynamics of circular dichroism (CD) and optical rotatory dispersion (ORD) is investigated with field applied molecular dynamics simulation (FMD) in chiral (S)-CHBrClF and achiral water ensembles. Rosenfeld tensor symmetries show that femtosecond transients and steady state correlation functions are different in the chiral ensemble but identical in the achiral ensemble for right and left circularly polarised components of a laser.

1. Introduction

Circular dichroism (CD) and optical rotatory dispersion (ORD) are well known manifestations of optical activity [1–3] in chiral ensembles, and are usually studied in the visible and infrared, to about 600 cm^{-1} [4,5]. Recent advances [4,5] mean that far-infrared CD and ORD might soon become possible, opening an experimental route to the investigation of the fundamental rotation/translation dynamics of ORD and CD. This Letter anticipates this development by using field applied molecular dynamics simulation (FMD) [6–10] to investigate the interaction of a right and left circularly polarised (c.p.) laser with: (a) a chiral ensemble of (S)-CHBrClF molecules; (b) an achiral ensemble of water molecules. It is shown that in case (a) a range of FMD time autocorrelation functions (ACFs) and second order rise transients (RTs) are different and distinct for right and left c.p. radiation, and that in case (b), no difference of this type was observable within the "computer noise". For example, the rotational velocity and orientational ACFs [11,12]

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differ in case (a), showing respectively the presence of far-infrared and dielectric frequency CD and ORD respectively. In general the complete range of ACFs and RTs are different for right and left c.p. radiation interacting with the chiral ensemble. This is significant for femto- and picosecond scale transient analysis [13–16], and for Rayleigh/Raman optical activity [17,18] in the far-infrared range of frequencies.

As a check, no differences of this type are observed within the FMD uncertainty for case (b).

2. Interaction of radiation and ensemble – the torques

When the left or right c.p. laser interacts with an ensemble of either chiral or achiral molecules each molecule experiences a different torque. The essence of FMD [6–10] is to code in the torque for each of N molecules in the simulation at the appropriate point in the forces loop of a standard m.d. algorithm (of any type). The method is therefore generally applicable to a range of problems, and has already produced insights in non-linear optics [6–10,17–20]. For CD and ORD the torque is evaluated from the interaction energy

$$\Delta En = -{}^c\alpha_{ij}^{\pi}(-\omega, \omega)E_i^* B_j + \text{c.c.} , \qquad (1)$$

where $^e\alpha_{ij}^m$ is the complex Rosenfeld tensor [3,18,21], and E_i^* and B_j are electric and magnetic components of the c.p. laser. Here E_i^* denotes the complex conjugate of E_i, and standard tensor suffix notation is used. The torque corresponding to eq. (1) is

$$T_l = -\epsilon_{lij}\,{}^e\alpha_{ik}^m(-\omega,\omega)B_k E_j^* + \text{c.c.} , \qquad (2)$$

where ϵ_{lij} is the Levi-Civita symbol. The torque T_l is used in the FMD algorithm TETRA [22] with right (R) and left (L) components of E and B. The Rosenfeld term is developed as usual [1–3],

$$^e\alpha_{ij}^m = {}^e\beta_{ij}^m + i\,{}^e\gamma_{ij}^m , \qquad (3)$$

$$^e\gamma_{ij}^m = {}^e\gamma_{ij}^m + i\,{}^e\gamma_{ij}^{m\prime} , \qquad (4)$$

in the semi-classical theory of molecular property tensors at optical resonance [3,21,23,24]. In this theory, $^e\gamma_{ij}^m$ is responsible for ORD, and $^e\gamma_{ij}^{m\prime}$ for CD. Equations (3) and (4) are clearly valid across the complete range of electromagnetic frequencies. The Rosenfeld component tensors $^e\gamma_{ij}^m$ and $^e\gamma_{ij}^{m\prime}$ have specific symmetry properties [18,21] for each molecular point group. For the C_1 symmetry group of (S)-CHBrClF all nine components of $^e\gamma_{ij}^m$ are independent and non-zero and all switch sign between enantiomers. In the C_{2v} point group of water the diagonal components of $^e\gamma_{ij}^m$ vanish, and if the C_{2v} axis is labelled 1 (the dipole axis) in the frame (1, 2, 3) of the point group, only $^e\gamma_{23}^m{}_* \neq {}^e\gamma_{32}^m$ off-diagonals are non-zero [18].

Taking (1, 2, 3) both for (S)-CHBrClF and water to be the frame of the principal molecular moments of inertia gives the torques in this frame respectively as the phase independent quantities.

2.1. (S)-CHBrClF

2.1.1. Left c.p. laser

$$T_1^L = -E_0 B_0 [2({}^e\gamma_{22}^m - {}^2\gamma_{33}^m)(e_{2X}e_{3X} + e_{2Y}e_{3Y})$$
$$+ ({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{2z}^2 - e_{3z}^2)$$
$$+ ({}^e\gamma_{12}^m + {}^e\gamma_{21}^m)(e_{3X}e_{1X} + e_{3Y}e_{1Y})$$
$$- ({}^e\gamma_{31}^m + {}^e\gamma_{13}^m)(e_{1X}e_{2X} + e_{1Y}e_{2Y})] ,$$

$$T_2^L = -E_0 B_0 [2({}^e\gamma_{33}^m - {}^e\gamma_{11}^m)(e_{3X}e_{1X} + e_{3Y}e_{1Y})$$
$$+ ({}^e\gamma_{31}^m + {}^e\gamma_{13}^m)(e_{3z}^2 - e_{1z}^2)$$
$$+ ({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{1X}e_{2X} + e_{1Y}e_{2Y})$$
$$- ({}^e\gamma_{12}^m + {}^e\gamma_{21}^m)(e_{2X}e_{3X} + e_{2Y}e_{3Y}) ,$$

$$T_3^L = -E_0 B_0 [2({}^e\gamma_{11}^m - {}^e\gamma_{22}^m)(e_{1X}e_{2X} + e_{1Y}e_{2Y})$$
$$+ ({}^e\gamma_{12}^m + {}^e\gamma_{21}^m)(e_{1z}^2 - e_{2z}^2)$$
$$+ ({}^e\gamma_{31}^m + {}^e\gamma_{13}^m)(e_{2X}e_{3X} + e_{2Y}e_{3Y})$$
$$- ({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{3X}e_{1X} + e_{3Y}e_{1Y})] . \qquad (5)$$

2.1.2. Right c.p. laser

$$T_1^R = -T_1^L, \quad T_2^R = -T_2^L, \quad T_3^R = -T_3^L . \qquad (6)$$

2.2. Water

2.2.1. Left c.p. laser

$$T_1^L = -({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{2z}^2 - e_{3z}^2)E_0 B_0 ,$$

$$T_2^L = -({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{1X}e_{2X} + e_{1Y}e_{2Y})E_0 B_0 ,$$

$$T_3^L = ({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)(e_{3X}e_{1X} + e_{3Y}e_{1Y})E_0 B_0 . \qquad (7)$$

2.2.2. Right c.p. laser

$$T_1^R = T_1^L, \quad T_2^R = -T_2^L, \quad T_3^R = -T_3^L . \qquad (8)$$

3. FMD methods

These torques were coded into frames (1, 2, 3) of each of 108 molecules of (a) (S)-CHBrClF, and (b) water, and back transformed [19,20,22] to the laboratory frame (X, Y, Z). The interaction site–site potentials (Lennard-Jones and partial charges) are described in the literature [25,26] in both cases. There appear to be no ab initio or experimental estimates of the individual scalar components of $^e\gamma_{ij}^m$ either in case (a) or (b). Accordingly, the arbitrary ratios

$${}^e\gamma_{11}^m : {}^e\gamma_{22}^m : {}^e\gamma_{33}^m : {}^e\gamma_{12}^m : {}^e\gamma_{21}^m : {}^e\gamma_{13}^m : {}^e\gamma_{31}^m : {}^e\gamma_{23}^m : {}^e\gamma_{32}^m$$

$$=7:8:9:1:2:3:4:5:6 \tag{9}$$

were used in case (a) and the product $({}^e\gamma_{23}^m + {}^e\gamma_{32}^m)E_0B_0$ given a numerical value in case (b).

After switching on the torques at an instant $t=0$, second order orientational RTs of the type

$$\langle e_{1X}^2 \rangle, \langle e_{1Y}^2 \rangle, \langle e_{1Z}^2 \rangle, ..., \langle e_{3Z}^2 \rangle$$

were evaluated over 2000 time steps, of 5.0 fs in case (a) and 0.5 fs in (b). Here e_{1X} for example denotes the X laboratory frame component of the unit vector e_1 in axis 1 of frame (1, 2, 3). The final levels attained by the transients were used to construct [6,19,20,22] Langevin Kielich functions as described in the literature. After attaining the post-transient steady state, laboratory frame ACFs were computed over a span of 6000 time steps for right and left c.p. torques in both cases. The following exemplify the data bank of ACFs from this work,

$$C_{1ij}(t) = \frac{\langle J_i(t)J_j(0)\rangle}{\langle J_i^2\rangle^{1/2}\langle J_j^2\rangle^{1/2}},$$

$$C_{2ij}(t) = \frac{\langle e_{1i}(t)e_{1j}(0)\rangle}{\langle e_{1i}^2\rangle^{1/2}\langle e_{1j}^2\rangle^{1/2}},$$

$$C_{3ij}(t) = \frac{\langle \dot{e}_{1i}(t)\dot{e}_{1j}(0)\rangle}{\langle \dot{e}_{1i}^2\rangle^{1/2}\langle \dot{e}_{1j}^2\rangle^{1/2}}. \tag{10}$$

These are respectively the angular momentum, orientational, and rotational velocity normalised ACF tensors. The second is essentially the Fourier transform [27,28] of the dielectric complex permittivity, and the third is the Fourier transform of the far-infrared power absorption coefficient in neper cm^{-1} [27,28]. Far-infrared CD measures the difference in this quantity from right and left c.p. probe radiation, either with a submillimetre laser [29] or with an interferometer [30].

4. Results and discussion

For cases (a) and (b) data banks were constructed of RTs and ACFs for several different values of E_0B_0. It was checked that the final levels reached by the FMD transients fell on the appropriate Langevin Kielich functions [12,20,31] using
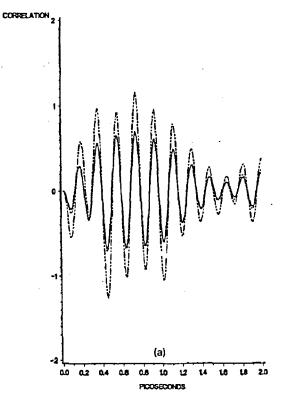
literature techniques [19,20,22] that we have developed for non-linear optics in general. For case (a) the second order RTs from torque (5) are different for right and left c.p. radiation. (The latter may be monochromatic or broad-band, because the torque is independent of the phase of the plane wave. The Rosenfeld tensor depends on frequency, however, in perturbation theory [3,16,21], so that the use of constant ${}^e\gamma_{ij}^m$'s means that we are effectively restricting our consideration to one frequency.) The RTs reach different saturation levels for right and left c.p. radiation, implying that the Langevin Kielich functions are also different. Figure 1 shows the same type of left/right difference in the ACF C_{3ij} of rotational velocity in case (a), a result which immediately shows the existence of far-infrared CD and ORD. Changing the numbers in eq. (9) changes the details of the left and right ACFs, as expected, but not the fact that they are distinct functions. In other words, changing the details of the Rosenfeld tensor does not eliminate the computed far-infrared ORD and CD.

Right and left torques make no difference, however, in case (b), either to RTs or ACFs exemplified by an angular momentum ACF. Clearly, the Langevin Kielich functions for water are also identical, analytically and computationally.

It is concluded that:

(1) FMD simulation in case (a) has revealed the presence of CD and ORD in the far-infrared and dielectric range of frequencies, showing that novel ACFs of the molecular dynamics of chiral molecules are all different for right and left c.p. radiation.

(2) FMD simulation in case (b) shows that there is a novel orientational anisotropy produced in an achiral ensemble by the Rosenfeld tensor's surviving off diagonal elements, but that there is no CD or ORD because left and right c.p. radiation components have identical dynamical effects.

(3) Novel second order RTs and Langevin Kielich functions in case (a) are different for left and right c.p. radiation, but the same in case (b).

Overall, this work has revealed for the first time the fundamental picosecond time scale, far-infrared frequency range, dynamical details of the way in which circularly polarised radiation interacts with a molecular ensemble through the mediating Rosenfeld tensor (or electric/magnetic dipole tensor). Clearly, it is important to note that the latter exists
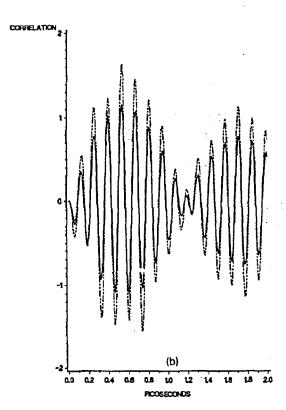
Fig. 1. Rotational velocity difference ACFs for (a) left, (b) right c.p. lasers applied to liquid (S)-CHBrClF, showing the FMD simulation of far-infrared CD and ORD. (——) C_{3XX}, (---) C_{3YY}, (—·—··—··) C_{3ZZ}. The laser propagates along the Z axis, and the Fourier transform of the component ACFs are far-infrared power absorption coefficients. (Field = 100 (a), 200 (b).)

in achiral as well as chiral ensembles, something which is overlooked frequently, but which has led to the new achiral birefringence phenomenon (2) above.

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