On electrostatic chiral discrimination

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In this paper, the roles of interbond angles, bond lengths, and electric charges in intermolecular electrostatic Chiral Discrimination (ChD) in the regimes of high temperature T and large intermolecular distance D are investigated. When both interacting molecules have asymmetries involving only interbond angles, or bond lengths, or charges, ChD varies as D^{-17}, D^{-21}, D^{-24}, respectively. In addition, ChD due to dispersion forces is studied. Given the popularity of computer calculations, the estimation of ChD between the various types of molecules can be used as a testbed for accuracy.

1. Introduction

The study of chiral molecules has been under greater and deeper scrutiny with each advance in biotechnology and drug research [22,30]. A molecule is chiral when its mirror image (i.e., enantiomer) is not superimposable on the original molecule. The interaction between two chiral molecules usually becomes different when one of the molecules is replaced by its enantiomer. This interaction difference is the basis of Chiral Discrimination (ChD) which can appear as a difference in energy levels [29], in the rotation of linearly polarized radiation [21], in physiological effects [23,30], in thermodynamic properties [27], and in many other phenomena. Since taking the mirror image does not reverse the course of time, the nuclear weak force may be evaluated by ChD studies [17,20]. However, since the weak force has, at least on a short time scale, a much smaller effect on ChD than electrostatic (ES) and electrodynamic (ED) forces, the vast majority of current research is focused on the ES and ED aspects of ChD. Often, ChD effects are so small compared to experimental and computational errors that some studies [6,12,19] contradict others [5,10,11]. Thus, some finer points of ChD remain to be studied.

Recently, Salem et al. [26] studied ES ChD between two molecules whose asymmetries involved only the charges. ChD was evaluated as the difference in the Boltzmann averaged intermolecular energy. Each molecule has a methane-like skeleton, denoted as $CX_1X_2X_3X_4$, and rotates freely about the C atom which is fixed in space. The X_k's have different electric charges, the C–X_k bonds are all equal in length, and the angles between two bonds C–X_k and C–X_m are all $\arccos(-1/3) \approx 109.5°$. The

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C-to-C distance is D and large compared to the C–X bond lengths. For a temperature T such that $k_{\mathrm{B}}T$ is much greater than the dipole–dipole interaction ($k_{\mathrm{B}} =$ molecular Boltzmann gas constant) and for 3 different values of D, ChD was evaluated numerically. With non-convergence for the smallest D, Salem concluded that ChD appeared to vary as D^{-22}. Previous theoretical studies [7–9] of classical (i.e., non-quantum) ES ChD showed that in general it varies as D^{-17}; however, the roles in ChD of asymmetries due to charges, bond lengths, and interbond angles were not investigated. In the numerical study [26], the precision (20 significant figures) and the large number ($\approx 10^7$) of relative intermolecular orientations for each D are such that one concludes beyond reasonable doubt that ChD does not vary as D^{-17} for the above-mentioned molecules. Arguments are presented here to indicate that, in the above case, ChD varies as D^{-24}.

Recently, Andelman et al. [1–3] studied ChD, due to dispersion forces characterized by the Lennard-Jones (LJ) potential, between two methane-like molecules of the $CX_1X_2X_3X_4$ type whose asymmetries are due partially to bond length difference. Each X_k has zero electric charge but different non-zero LJ parameters ε_k and σ_k; the angles between C–X_k and C–X_m bonds are all 109.5°. The LJ energy potential E_{LJ} between X_k and X_m separated by distance D is [3]

$$E_{\mathrm{LJ}} = 2(\varepsilon_k\varepsilon_m)^{1/2}\big[\big((\sigma_k+\sigma_m)/D\big)^{12} - 2\big((\sigma_k+\sigma_m)/D\big)^{6}\big]. \tag{1.1}$$

Although ChD was evaluated for D, large and small, with about 10^7 possible relative intermolecular orientations used for each value of D, Andelman stated that the calculations were not precise enough to yield reliable measure of ChD. One shows that, for the molecules considered by Andelman, ChD varies as D^{-36}.

One focuses on asymmetric molecules/ions with 3 charges since, as long as translation is forbidden, 3 charges is the minimum to demonstrate ChD in the freely rotating case. If translation is allowed, 4 charges are necessary [31]. The charge distribution of each molecule in the studies of [1–3,26] can be seen as a set of 4 triads (($X_1X_2X_3$), ($X_1X_2X_4$), ($X_1X_3X_4$), ($X_2X_3X_4$)) which interacts with the set of triads of the other molecule; ChD is shown [26] to be due mainly to these inter-triad interactions. Each molecule/ion rotates freely, its center of rotation being fixed in space, has pointlike charges, and has zero polarizability. D is the distance between the two centers of rotation. The radii, or bonds, are line segments of constant lengths (no stretching vibrational modes) connecting the charges to the rotation center. The bond lengths are of the same order of magnitude and D is considered large when D is greater than 10 times the average bond length. The angles between two given radii are constant (no bending vibrational modes). Although the term molecule is used generally for chemical species with zero net charge, the term will be used in this paper to include ions.

2. Overview of necessary conditions for thermodynamic ES ChD

A measure of ChD can be ΔE_{aA} [7–9],

$$\Delta E_{aA} = \langle V(a,A)\rangle - \langle V(a,A^*)\rangle = -\Delta E_{aA^*} = -\Delta E_{a^*A}. \tag{2.1}$$

Molecules a and A are chiral; A^* is the enantiomer of A. $V(a,A)$ is the ES potential between the molecular pair (a,A) and is given as [14]

$$V(a,A) = \sum_{n=0}^{\infty}\sum_{N=0}^{\infty}\sum_{m=-n_<}^{n_<} C(n;N;m)q_a(n;m)q_A(N,-m)D^{-n-N-1}, \tag{2.2}$$

$$C(n;N;m) = \frac{(-1)^{n+m}(n+N)!}{(n+|m|)!(N+|m|)!}; \tag{2.3}$$

$n_<$ is the smaller of the two integers n and N, $q_x(n,m)$ is the laboratory-fixed multipole of molecule x, of principal and orbital numbers n and m, respectively, and changes with different molecular orientations. Since $C(n;N;m) = C(n;N;-m)$, the imaginary part of $q_a(n,m)q_A(n,-m)$ cancels out the imaginary part of $q_a(n,-m)q_A(n,m)$ and, thus, $V(a,A)$ has no imaginary part overall. $\langle V(a,A)\rangle$, equal to $-(\partial \ln Z(a,A)/\partial\beta)$, is the Boltzmann-weighted average of $V(a,A)$. $\beta = (k_{\mathrm{B}}T)^{-1}$ and $Z(a,A)$ is the partition function:

$$Z(a,A) = \iint \exp\bigl[-\beta V(a,A)\bigr]\,\mathrm{d}\omega_a\,\mathrm{d}\omega_A. \tag{2.4}$$

$\mathrm{d}\omega_x$ denotes the set of increments in the 3 Euler angles of molecule x; the integrals in or A. Henceforth, the subscript x denotes either molecule a or A. The integrals in (2.4) are over all possible ranges of angles. In the high T, large D regime one has $\beta V(a,A) \ll 1$ and $\langle V(a,A)\rangle$ can be written as a formal power series in β:

$$\langle V(a,A)\rangle = \sum_{k=0}^{\infty}\beta^k \mathcal{V}_{aA;k}. \tag{2.5}$$

The ChD discussion boils down to the analysis of the $\mathcal{V}_{aA;k}$ terms which have been studied to some depth by others [7–9] and which are proportional to

$$\left[\prod_{s=0}^{k} Q_a(n_s,l_s)\right]\left[\prod_{t=0}^{k} Q_A(n_t,l_t)\right] D^{-(k+1)-\mathcal{N}(a)-\mathcal{N}(A)}, \tag{2.6}$$

$$\mathcal{N}(x) = \sum_{b=0}^{k} n_b. \tag{2.7}$$

$Q_x(n,l)$ is the molecule-fixed multipole moment of principal number n and orbital number l for molecule x. $\mathcal{N}(x)$ relates to molecule x. The n_b's in (2.7) are the principal numbers for the $Q_x(n,l)$'s in (2.6).

The laboratory-fixed multipoles $q_A(n,m)$ vary as the molecular orientations change. The molecule-fixed multipoles $Q_A(n,l)$ are independent of molecular orientation with respect to the laboratory coordinate system. $Q_A(n,l)$ and $q_A(n,m)$ are related via the rotation functions $\mathcal{D}(n;m,l)$ which are functions of the Euler angles of molecular rotation [7–9]. The following conditions (2.8), (2.9) are conditions for the rotational averages of the products of $\mathcal{D}(n;m,l)$ to be non-zero. The necessary ChD conditions are [9]

$$\mathcal{L}(x) = \sum_{s=0}^{k} l_s = 0, \tag{2.8}$$

$$\sum_{s=0}^{k-1} n_s \geqslant n_k, \quad \text{if } n_h \geqslant n_j \text{ when } h > j, \tag{2.9}$$

$$\mathrm{Im}\left[\prod_{s=0}^{k} Q_x(n_s, l_s)\right] \neq 0, \tag{2.10}$$

$$\mathcal{N}(x) = \sum_{b=0}^{k} n_b = \text{odd integer}. \tag{2.11}$$

$\mathcal{L}(x)$ relates to molecule x and the l_s's in (2.10) are the orbital numbers for the $Q_x(n,l)$'s in (2.8). Further discussion of (2.9) is given by previous authors [9,25]. If there is an orientation of axes such that (2.10) is violated, ChD does not appear in the term under question. Thus the discussion boils down to finding any orientation to make (2.10) non-valid; if no such orientation exists, then ChD is present.

3. A novel orientation of molecule-fixed coordinates

To understand the role of charges, bond lengths, and interbond angles in ChD, a novel coordinate orientation with respect to a molecule is used. One aligns the z-axis ($\theta = 0$ line) along vector $\vec{S}$,

$$\vec{S} = \left[\left(\widehat{r}_1 \times \widehat{r}_2\right) + \left(\widehat{r}_2 \times \widehat{r}_3\right) + \left(\widehat{r}_3 \times \widehat{r}_1\right)\right], \tag{3.1}$$

instead of doing the usual alignment along the molecular dipole moment. $\widehat{r}_y = \vec{r}_y/|\vec{r}_y|$, the subscript y being 1, 2, or 3. The coordinate origin is collocated with the center of rotation. Since

$$\left(\widehat{r}_1 \cdot \vec{S}\right) = \left(\widehat{r}_2 \cdot \vec{S}\right) = \left(\widehat{r}_3 \cdot \vec{S}\right) = \left(\widehat{r}_1 \cdot \widehat{r}_2 \times \widehat{r}_3\right), \tag{3.2}$$

then $\theta_1 = \theta_2 = \theta_3$ and the $P_n^m(\cos\theta)$'s can be ignored in the ChD discussion. Differences $(\phi_k - \phi_m)$ in the azimuthal coordinates reflect differences in $(\widehat{r}_k \cdot \widehat{r}_m)$, the subscripts k and m being 1, 2, or 3.

4. Characterization of 3-Charge Molecules (3CM)

To understand the role of charges, bond lengths, and interbond angles in ChD, 3CM's are characterized in terms of the number of inequalities amongst their structural parameters. The degree of asymmetry may be characterized by the number of inequalities between interbond angles (A), bond lengths (R), and charges (C). If the interbond angles X_k–C–X_m are all equal, then the 3CM has an A_0 character since there are no inequalities between the angles; if the angles are all different from one another, then the 3CM has an A_3 character since there are 3 inequalities: angle(X_1–C–X_2) $\neq$ angle(X_2–C–X_3) $\neq$ angle(X_1–C–X_3) $\neq$ angle(X_1–C–X_2).

Since a 3CM can be only A_0, A_2, and A_3 (analogously for bond lengths and charges), there are 27 types ($A_xR_yC_z$) of 3CM's. Because 3CM's of type $A_0R_0C_0$, $A_2R_0C_0$, $A_0R_2C_0$, $A_0R_0C_2$ are achiral, there are 23 types of asymmetric 3CM's (A3CM). One notes there are chiral and achiral 3CM's of types $A_2R_2C_0$, $A_2R_0C_2$, $A_0R_2C_2$, and $A_2R_2C_2$.

5. Thermodynamic ES ChD between two A3CM's

In the following, one uses the definition [14]

$$Q_x(n,m) = \sum_{s=1}^{3} e_s r_s^n P_n^m(\cos\theta_s)\exp(\mathrm{i}m\phi_s). \tag{5.1}$$

e_s and r_s are, respectively, the sth charge and the (center of rotation)–(sth charge) distance. $P_n^m(\cos\theta)$ is an associated Legendre function. One writes out the left-hand side of (2.9) in terms of its charge (e_s), bond length (r_s), and interbond angle (θ_s) components. After permuting a pair of indices of the bond length components (for the $A_0R_3C_0$, $A_0R_2C_2$ molecules), or of the charge components (for the $A_0R_0C_3$, $A_0R_2C_2$ molecules), one ascertains if the permutation changes the value of said terms. Since permuting a pair of indices is akin to producing the enantiomer, if permuting any pair of indices leaves a term unchanged, then the said term does not contribute to ChD.

For a pair of interacting $A_3R_0C_0$ molecules, ChD first occurs in terms of type (2.10) such as

$$Q_a(2,-1)Q_a(2,-1)Q_a(3,2)Q_A(2,-1)Q_A(2,-1)Q_A(3,2)D^{-17}. \tag{5.2}$$

The ChD part in $Q_a(2,-1)Q_a(2,-1)Q_a(3,2)$ varies as

$$\left(e_1^3 r_1^7\right)\sum_{k=1}^{3}\sum_{p=1}^{3}\sum_{t=1}^{3}\mathcal{M}_{kpt}\exp\left[\mathrm{i}(2\phi_t-\phi_p-\phi_k)\right], \tag{5.3}$$

where $\mathcal{M}_{kpt} = 1$ when $k \neq p \neq t \neq k$, and 0 otherwise. Setting $\phi_1 = 0$, having $-\pi < \phi_t < \pi$ for $t = 2, 3$, and recalling (2.9), one finds the imaginary part of (5.3) to vary as

$$2\sin\big[(1/2)(\phi_2 + \phi_3)\big]\cos\big[(3/2)(\phi_2 - \phi_3)\big] - \sin(\phi_2 + \phi_3). \tag{5.4}$$

If two interbond angles are equal (thus, not $A_3R_0C_0$) the molecular coordinate system can be such that $(\phi_2 + \phi_3) = 0$, making (5.4) zero, implying no ChD. For $A_3R_0C_0$ molecules, $(\phi_2 + \phi_3) \neq 0$ always as long as $\phi_1 = 0$. To produce the enantiomer one reflects molecule a with respect to the plane containing $\vec{S}$ and $\vec{r}_1$, thus keeping ϕ_1 zero and reversing the signs of ϕ_2 and ϕ_3; consequently (5.4) changes sign, thus demonstrating ChD.

For a pair of $A_0R_3C_0$ molecules, the leading ChD terms arise not from (5.2), since permuting indices k and p leaves $(r_k^2 r_p^2 r_t^3)$ unchanged, but from terms such as

$$Q_a(2,-1)Q_a(3,-1)Q_a(4,2)Q_A(2,-1)Q_A(3,-2)Q_A(4,3)D^{-21}, \tag{5.5}$$

since permuting any pair of indices changes the value of $(r_k^2 r_p^3 r_t^4)$.

For a pair of $A_0R_2C_2$ molecules, where molecule A (and a) is such that $r_1 = r_2 \neq r_3$ and $e_1 \neq e_2 = e_3$, ChD first arises from terms such as

$$Q_a(1,0)\big[Q_a(2,-1)\big]^2 Q_a(2,2)Q_A(1,0)\big[Q_A(2,-1)\big]^2 Q_A(2,2)D^{-18}, \tag{5.6}$$

which contains factors proportional to $[(e_1^2 e_2 e_3)(r_1^4 r_2^2 r_3)]$ which changes value for any permutation of a pair of indices.

If molecule a is of the $A_3R_0C_0$ type and molecule A of the $A_0R_3C_0$ type, ChD first arises in terms such as

$$Q_a(2,-1)Q_a(2,-1)Q_a(3,2)Q_A(2,-1)Q_A(3,-2)Q_A(4,3)D^{-19}. \tag{5.7}$$

For a pair of interacting $A_0R_0C_3$ molecules, leading ChD terms arise from terms such as

$$\big[Q_a(1,0)\big]^3\big[Q_a(2,-1)\big]^2 Q_a(2,2)\big[Q_A(1,0)\big]^3\big[Q_A(2,-1)\big]^2 Q_A(2,2)D^{-24}. \tag{5.8}$$

Expression (5.8) contains terms proportional to $(e_k e_p^2 e_t^3)$ which changes value for any given permutation of pairs of indices, since in the current case, $e_1 \neq e_2 \neq e_3 \neq e_1$. Returning back to [26], one sees that each triad of each molecule is of the $A_0R_0C_3$ type and that ChD varies as D^{-24} because, since no triad is the enantiomer of another, the sum of the ChD terms is non-zero generally. Leading ChD terms involving all 4 charges simultaneously (i.e., not derivable simply from intertriad interactions) occur in $\mathcal{V}_{aA;9}$, contain terms in $(e_k e_p^2 e_t^3 e_u^4)$, and vary as D^{-36}. In the large D limit, $D^{-36} \ll D^{-24}$, confirming the earlier statement that intertriad interactions give the large D behavior of ChD.

6. Thermodynamic ChD due to dispersion forces

In the following, one rewrites the intermolecular interaction due to the LJ potential in a framework similar to that presented for the ES interaction. Since, for a given atom f, there are two LJ potential parameters ε_f and σ_f, the molecular multipoles related to the dispersion forces involve various combinations of ε_f and σ_f. In addition, since one is interested in the large D regime, only the attractive part of the LJ potential is relevant in the following. Suppose atom f of molecule a interacts with atom F of molecule A. $\vec{D}$ is the vector originating from the center of rotation of molecule A and terminating at the center of rotation of molecule a. Thus the reciprocal of the distance R_{fF} between atoms f and F is given by

$$(R_{fF})^{-1} = \sum_{n=0}^{\infty}\sum_{N=0}^{\infty}\sum_{u=-n_<}^{n_<} C(n;N;u)\mathfrak{q}_f(n,u)\mathfrak{q}_F(N,-u)D^{-n-N-1}, \tag{6.1}$$

$$R_{fF} = \left|\vec{r}_f + \vec{D} - \vec{r}_F\right|, \tag{6.2}$$

$$\mathfrak{q}_x(n,m) = P_n^m(\cos\theta_x)\exp(\mathrm{i}m\phi_x). \tag{6.3}$$

The factors $C(n;N;u)$ in (6.1) are complicated functions and are not essential in the discussion. The attractive part of the LJ potential is

$$(R_{fF})^{-6} = \sum_{n=0}^{\infty}\sum_{N=0}^{\infty}\sum_{r=-n_<}^{n_<}\sum_{s=0}^{\infty}\mathfrak{q}_f(n,r)\mathfrak{q}_F(N,-r) \times B(n,N,r,s)D^{-n-N-6-s}. \tag{6.4}$$

Since one is interested in the leading ChD terms, one focuses here only on the terms where $s = 0$ in (6.4). Then the intermolecular LJ potential $V_{\mathrm{LJ}}(a,A)$ can be approximated as

$$V_{\mathrm{LJ}}(a,A) \approx \sum_{n=0}^{\infty}\sum_{N=0}^{\infty}\sum_{m=-n_<}^{n_<}\sum_{v=0}^{6}\mathcal{Q}_a(n,m,v)\mathcal{Q}_A(N,-m,6-v) \times B(n,N,m,0)D^{-n-N-6}, \tag{6.5}$$

$$\mathcal{Q}_x(n,m,v) = \binom{6}{v}^{1/2}\sum_{s=1}^{3}(2\varepsilon_s)^{1/2}\sigma_s^v\mathfrak{q}_s(n,m). \tag{6.6}$$

In (6.6), s ranges from 1 to 3, because one is still considering 3CM's where each electric charge is replaced by an atom with its two LJ parameters. The lessons learned in the previous sections can be extended easily to the current LJ potentials. Where the ES ChD arising from the product of (h) Q_A's varies as D^{-y}, the corresponding LJ ChD varies as $D^{-y-5(h)}$. For illustration, one returns to [3]; the triads under study are of the $A_0R_3C_3$ type, thus LJ ChD varies as $D^{-21-5(3)} = D^{-36}$.

7. Conclusion

The above algebraic treatment presents useful qualitative results, namely that interbond angle differences have a greater influence on ChD than bond length differences which, in turn, have a greater influence on ChD than charge differences. These qualitative results are not easily deduced from intuition alone; otherwise, previous ChD studies would have looked at $A_3R_*C_*$ molecules instead of $A_0R_0C_3$ or $A_0R_3C_3$ molecules (subscript $*$ denotes 0, 2, or 3). The above results can be used to study dilute gases composed of chiral molecules and dilute solutions of electrolytes composed of chiral anions (conjugate bases of chiral carboxylic acids, for example) or chiral cations (chiral quartenary ammonium ions, for example). Two chiral cations (or two chiral anions) in solution repel one another and the large D results may apply. By breaking down multi-charged molecule/ions into a set of triads, one can easily investigate ChD between various types of, say, chiral fullerene cages which have been the focus of recent investigations [4].

Although neither the present study nor prior work investigated the specific role of vibrational modes in intermolecular ChD, one expects bending modes to be more important than stretching modes in affecting ChD, since a molecule can become of the $A_3R_*C_*$ type via bending modes; one find analogous results for radiation–molecule interactions: studies of vibrational circular dichroism of propylene oxide [18,24] and theoretical work [15] on NHDT showed that bending modes have much larger rotational strengths than stretching modes. Also, since bond length differences have greater importance in ChD than charge differences, one expects molecular quantum electronic transitions, which leave internuclear distances unchanged, to have a much smaller role in affecting ChD than vibrational modes; one finds analogous results for radiation–molecule interactions: in the theory of dispersion-induced circular dichroism [28], vibronic state transitions play a much greater role than pure electronic state transitions. Thus, although there may not be a unified mode of physical chiral measure [13], further work on the decomposition of asymmetry into its various components (charge, nuclear mass, bond lengths, interbond angles, etc.) may reveal some simple chiral measures which encompass a large fraction of physical phenomena.

One can extend the above results to the case of polarizable molecules, where the molecule-fixed multipoles are functions of the relative orientation of the molecules. A perturbative study involves derivatives of the multipoles with respect to bond lengths and azimuthal and polar angles; these derivatives can be expressed in terms of "multipoles" involving 3 charges/polarizabilities if the molecules have at least 4 non-central charges. The ChD analysis boils down to studying products of molecule-fixed "multipoles". One easily finds temperature-independent electrostatic ChD between polarizable molecules. Recently, ChD due to electric and magnetic multipole interactions has been studied in the framework of quantum electrodynamics [16]; ChD is found to vary as D^{-8} and has yet to be confirmed experimentally. Nonetheless, the role the asymmetries involving angles, bond lengths and charges has not been scrutinized in [16] and numerical studies involving the analysis of [16] may be most illuminating.

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