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DIFFERENTIATION OF OPTICAL ISOMERS THROUGH ENHANCED
WEAK-FIELD INTERACTIONS

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ABSTRACT

Cooperative effects arising from the contributions of a macroscopic assemblage of interacting sites will greatly magnify the influence of weak-field interaction terms. As a result, significant differential adsorption of optical isomers onto an achiral surface is predicted to occur if the surface is continuous and sufficiently large.

I. Introduction

The possibility that achiral surfaces, such as clay surfaces, may still differentiate between optical isomers has intrigued researchers and has been the motivation for numerous investigations [1,2,3,4]. The results to date have been ambiguous. A theoretical framework, which could be used to decide whether or not a set of experiments might be successful or even delineate the minimal conditions necessary for success, has been lacking. It is the purpose of this communication to provide a possible theoretical model for the resolution of enantiomers by achiral surfaces.

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The question of chirality has been subjected to reexamination recently in two very different approaches. The first adopts Hund's explanation [5] but appends weak-field interactions to it. The second rejects Hund's explanation and replaces it with a possibly more fundamental one [6]. Weak-field interactions are not included in Pfeifer's [6] treatment, but such inclusion is thought to be straightforward. The importance of the weak-field interactions are that they break the degeneracy between optical isomers to a miniscule extent, generally. We will argue that there are cases where the effects will not be insignificant. Thus the opening remarks in this paragraph are important in establishing that effects arising from weak-field interactions are not dependent on the particular model of chirality. The extent to which the degeneracy between optical isomers is split may be model-dependent, however. The discussion of the weak-field interaction begins with the formal expression obtained by Bouchiat and Bouchiat [7].

II. Weak-Field Interaction Terms

Nonvanishing contribution to the parity nonconserving energy arises in second order when spin-orbit coupling is included. Approximating the ground state and excited wavefunctions of a molecular system by single determinants of molecular orbitals yields, following Rein et al. [8], the pnc energy

$$\delta\omega = \sum_{f,e} \frac{\langle \phi_f \chi_f | H^{\text{pnc}} | \phi_e \chi_e \rangle \langle \phi_e \chi_e | H^{\text{SO}} | \phi_f \chi_f \rangle}{\omega_f - \omega_e} + \text{c.c} \quad (1)$$

The (χ) terms are spin functions while f denotes filled orbitals and e denotes empty ones. Summing over the spin magnetic quantum numbers in equation (1) reduces the expression to the spin-independent form (from Rein et al. [8]).

$$\delta\omega = 2\Sigma \frac{\langle \phi_f | \hat{N} | \phi_e \rangle \langle \phi_e | \hat{A} | \phi_f \rangle}{\omega_f - \omega_e} + \text{c.c.} \quad (2)$$

Here \hat{N} and \hat{A} are the appropriate operators obtained from H^{pnc} and H^{so} , respectively, upon suppression of the spin operators. The molecular orbitals are assumed to be expressible as LCAOs where

$$\phi_f = \Sigma_i \Sigma_{k(i)} c_{f,k(i)} \psi_{k(i)} \quad (3)$$

The $\psi_{k(i)}$ are atomic orbitals associated with the i th atomic center and the $c_{f,k(i)}$ are the appropriate coefficients of the $\psi_{k(i)}$ in the f molecular orbital. Again following Rein et al. [8], overlap is neglected and each matrix element in equation (2) is restricted to a single center. Then, with use of equation (3), equation (2) yields

$$\delta\omega = 4 \Sigma_{f,e} \Sigma_{i,r} \Sigma_{k(i),l(i)} \Sigma_{u(r),v(r)} c_{f,k(i)} c_{e,l(i)} c_{f,u(r)} c_{e,v(r)} \times \frac{\langle \psi_{k(i)} | \hat{N} | \psi_{l(i)} \rangle \langle \psi_{u(r)} | \hat{A} | \psi_{v(r)} \rangle}{\omega_f - \omega_e} \quad (4)$$

As Rein, et al. noted [8], $\delta\omega = 0$ if $i = r$. The importance of the expression in equation (4) is its generality. It is not restricted to simple molecules but can be applied equally well to extensive multicenter interacting systems such as crystals. For such a system, the atomic orbitals from which the molecular orbitals are constructed are dispersed throughout and

include the entire crystal. Thus equation (4), in this context, leads to the implication that cooperative effects are operating in a giant molecule with many sites. As a consequence, all sites (assuming that each site experiences some degree of asymmetry in its environment) contribute to the energy $\delta\omega$ in such a fashion that there can be no reduction of the double summation over those sites. The operators \hat{N} and \hat{A} are preferentially weighted toward those regions close to "heavy" nuclei. Accordingly, if all sites are identical and each contains one "heavy" atom (such as silicon) and there are N sites, then, for those molecular orbitals whose composition includes orbitals associated with the i th "heavy" nuclear center, the coefficients of these atomic orbitals are

$$|c_{f,k(i)}| \propto N^{-1/2}$$

$$|c_{e,l(i)}| \propto N^{-1/2}.$$

Furthermore, the sums in equation (4) for these molecular orbitals run over all N "heavy" centers. The number of molecular orbitals that contain atomic orbitals associated with the "heavy" nuclear centers is $O(N)$. Therefore, the weighted contribution from all the sites to a $\langle \dots \rangle \langle \dots \rangle$ term in equation (4) is $O(1)$.

The unperturbed energy for the system, relating it to an energy, ϵ , associated with a hypothetical isolated site, is set equal to

$$\omega = N\epsilon.$$

Similarly, if we denote by $\delta\epsilon$ the value of the average weak-field interaction term that can be assigned to the hypothetical isolated site, examination of

equation (4) suggests that the second-order perturbation term equals

$$\delta\omega \approx N^2 \delta\epsilon.$$

Any proportionality constant has been absorbed in the $\delta\epsilon$. This relationship is supported upon noting that the sum over f, e orbitals in equation (4) involves $O(N^2)$ terms. Substitution of the denominator in equation (4) by $\langle \Delta\omega \rangle_{ef}$, where $\langle \Delta\omega \rangle_{ef}$ is the weighted difference of a representative subset of $(\omega_f - \omega_e)$ terms from the f and e bands, yields

$$\delta\omega \approx N^2 (4/\langle \Delta\omega \rangle_{ef}) \sum_{f^*, e^*} \sum_{i, r} \sum_{k(1), l(1)} \sum_{u(r), v(r)} c_{f^*, k(1)} c_{e^*, l(1)} \times c_{f^*, u(r)} c_{e^*, v(r)} \langle \psi_{k(1)} | \frac{A}{N} | \psi_{l(1)} \rangle \langle \psi_{u(r)} | \frac{N}{N} | \psi_{v(r)} \rangle. \quad (5)$$

Here the (f^*, e^*) sum is over an appropriate subset of f and e orbitals; these have been labeled f^* and e^* . Thus there appears to be an enhancement effect of $O(N)$ in a system comprised of N coupled sites. Consequently, this imposes a constraint on the second-order perturbation expression since equation (4) can only be assumed valid if $\omega \gg \delta\omega$. (In terms of our approximate expressions, $\epsilon \gg N\delta\epsilon$.) The following section will focus on the application to very large systems by using the techniques of statistical mechanics.

III. Application of the Weak-Field Interaction Perturbation

The magnitude of the weak-field terms for an isolated site is very small; estimates range from 10^{-21} au to 10^{-18} au [5,8]. Therefore, although it has been argued [9] that such infinitesimal differences cannot affect chemical processes, cooperative effects will profoundly alter this conclusion. We adopt a picture in which adsorption occurs from a solution

containing a racemic mixture (the optical isomers are hereafter noted as A and B) onto a continuous surface possessing N achiral sites, each of which has a "heavy" atom. It is assumed that all sites are occupied with either an A or a B isomer. The spin-orbit terms in equation (4) include all N sites. Two cases are considered. In the first case we assume that the adsorbed isomer introduces asymmetry into the environment of the "heavy" atom and it is also strongly coupled with the surface. In the second case, which is a limit of the first, we only assume that an asymmetry is introduced into the "heavy" atom environment. The first case will be treated in some detail since the results can be easily modified to yield the second-case limit. The energy difference between adsorption of the A isomer over the B form is given by

$$\begin{aligned} \Delta E &\approx N(\delta\epsilon_{\text{site}}^A - \delta\epsilon_{\text{site}}^B + \delta\epsilon_{\text{isomer}}^A - \delta\epsilon_{\text{isomer}}^B) \\ &\approx 2N(\delta\epsilon_{\text{site}}^A + \delta\epsilon_{\text{site}}^B) \end{aligned} \quad (6)$$

It is readily shown, if we assume that the Boltzmann distribution is applicable, that the partition function for this system equals

$$Q = \sum_{N_A=0}^N \frac{N!}{N_A! N_B!} \exp(-\beta N_A \Delta E) \exp \left[-\beta N^2 (\delta\epsilon_{\text{site}}^B + \delta\epsilon_{\text{isomer}}^B) \right]. \quad (7)$$

Here, $\beta = 1/kT$ where k is the Boltzmann constant and N is constrained by the requirement that

$$N = N_A + N_B. \quad (8)$$

The terms ΔE , $\delta\epsilon_{\text{site}}^B$, $\delta\epsilon_{\text{isomer}}^B$, and N are constants. Only N_A and N_B can vary; however, from the relationship in equation (8) the variation of N_A is

$$\delta N_A = -\delta N_B. \quad (9)$$

The most probable distribution of A and B is found by setting the variation of Q,

$$\delta Q = 0$$

and solving the resulting equation. This distribution, in terms of N_A and N_B , is found to equal

$$N_B/N_A = \exp(\beta\Delta E). \quad (10)$$

Suppose there are M isolated surfaces, each possessing N sites, which are simultaneously exposed to the same racemic solution. The most probable distribution is obtained by using the same procedure outlined previously. The result is identical to the relationship in equation (10), i.e.,

$$MN_B/MN_A = N_B/N_A = \exp(\beta\Delta E). \quad (11)$$

Thus the most probable distribution depends on the number of sites per surface. It depends on the total surface only if that total represents a single continuous surface. This result might be crucial in determining whether or not an experiment can yield detectable differential adsorption.

As an illustration, we assume that

$$\delta\epsilon_{\text{site}}^A \approx 10^{-23} \text{ au},$$

$$\delta\epsilon_{\text{isomer}}^A \approx 10^{-20} \text{ au}.$$

The value for $\delta\epsilon_{\text{site}}^A$ is chosen on the assumption that the estimate by Rein et al. [8] is representative for the situation in which asymmetry is introduced at a distance from the "heavy" atom. The value $\delta\epsilon_{\text{isomer}}^A$ is purposefully chosen two orders smaller than the upper-bound estimate (10^{-18} au)

for comparable systems since this upper bound is in question [8]. Then the number of sites a single surface (hereafter crystal and surface will be used interchangeably) must possess in order that there be a one-percent differentiation in the adsorption of B isomer with respect to A isomer can be determined by using equation (10). We desire that the ratio of the number of adsorbed A isomers to the number of adsorbed B isomers equal

$$N_B/N_A = 1.020.$$

Solving equation (10) for $\beta\Delta E$ yields

$$\beta\Delta E \approx 0.020.$$

Since

$$\Delta E \approx 2N \times 10^{-20} \text{ au},$$

then at 300°K the number of sites must equal

$$N \approx 1 \times 10^{18}.$$

In the second case, where the only effect of the optical isomers is to introduce asymmetry into the environment of the "heavy" atom, the expression in equation (6) now equals

$$\Delta E \approx 2N\delta\epsilon_{\text{site}}^A,$$

$$\Delta E \approx 2N \times 10^{-23} \text{ au},$$

from which we get

$$N \approx 1 \times 10^{21}.$$

If we assume an area of about 10 \AA^2 per site, which is a reasonable value for a representative SiO_4 unit in cristobalite, for example, then the minimum area that the single crystal surface must equal for a one-percent differential adsorption is given by

$$A_{\text{min}} \approx 1 \times 10^3 \text{ cm}^2 \text{ (first case),}$$

$$A_{\text{min}} \approx 1 \times 10^6 \text{ cm}^2 \text{ (second case).}$$

It is clear from equation (11) that a collection of smaller crystals whose total area equals A_{min} would not yield the one-percent differentiation since the percentage differentiation depends on the number of sites per crystal and not on the number of crystals.

IV. Conclusion

A cooperative effect is possible on a continuous surface with many available adsorption sites. Thus, even though the weak-field interaction terms are almost vanishingly small for one center, a cooperative effect can greatly magnify these miniscule energies. Results from a naive statistical mechanical treatment show that this amplification feature indeed can lead to the resolution of enantiomers by achiral surfaces. For purposes of laboratory demonstration, however, the minimum area that an achiral surface must have in order to effect a one-percent differentiation is sufficiently large, from estimates made in section III, that any experiment would be extremely difficult to execute properly. Since, as shown in the text, the quantity of discontinuous crystal surfaces does not enhance the percentage of differentiation, the standard procedure of using large quantities of small particles is

not a viable technique for obtaining a detectable ($\geq 1\%$) differentiation of optical isomers on an achiral surface. This latter observation may explain, to some degree, the ambiguous and often conflicting results obtained to date when such experiments have been attempted.

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