

## Parity-violating effects in asymmetric chemical reactions: A theoretical study on the CHFClBr molecule

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A coupled Hartree-Fock procedure has been employed to estimate the parity-violating energy contribution due to electroweak interaction in the vicinity of the transition point of a chemical reaction path starting from achiral reagents and producing the chiral CHFClBr molecule. The calculations demonstrate that (i) the *S* enantiomer is a reaction product more stable than its mirror image by  $\approx 1 \times 10^{-17}$  hartree; (ii) in the transition state of the reaction, the chiral activated complex evolving toward the *S*-CHFClBr species is more stable, by  $\approx 2.3 \times 10^{-17}$  hartree, than the enantiomeric activated complex that would yield the *R*-CHFClBr species. These results suggest that kinetic effects at work during chemical syntheses of chiral molecules might be more significant than the different thermodynamical stability of the two mirror-image reaction products in determining the final configuration and to explain homochirality.

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### I. INTRODUCTION: THE ORIGIN OF TERRESTRIAL HOMOCHIRALITY

The search for effects due to parity-violating electroweak forces at the molecular level has recently aroused increasing attention. Although the existence of parity-nonconserving interactions [1] has been experimentally proven in elementary particle physics, e.g., *P*-odd charged weak currents carried by  $W^\pm$  bosons determine the  $\beta$  decay of radionuclides [2], the signature of neutral weak currents mediated by the heavy  $Z^0$  boson in molecular physics and chemistry still needs to be unequivocally documented.

Atoms are handed, as can be directly measured by a number of experiments reported by many groups [3]. However, attempts made so far to detect any difference between the vibrational spectra of two enantiomeric molecules were not successful [4–9]. On the other hand, claims have been recently made that an enantiomeric excess arising from parity-violating forces appears in the crystallization process of cobalt and iridium complexes [10].

Different implications for homochirality have been proposed, e.g., a strong circularly polarized infrared light observed within the Orion OMC-1 star formation region could provide indicial evidence of circular polarization at shorter wavelengths, inducing chiral asymmetry in interstellar organic molecules [11]. Within another extraterrestrial scenario, the dominant enantiomeric species of terrestrial biochemistry might have been carried by comets [12].

The spin-polarized electrons produced in the  $\beta$  decay may cause preferential destruction of one enantiomer in a racemic mixture [13]. According to Ray *et al.* this mechanism may be effective through molecular orientation by absorption at an interface, due to asymmetric scattering of polarized electrons [14]. Excellent reviews became recently available, discussing the origin of homochirality [15], and the formation of enantiomeric excess upon irradiation [16].

### II. THEORETICAL ESTIMATES OF PARITY-VIOLATING ENERGY DIFFERENCES

So far the efforts of theoreticians have been mainly directed to evaluating the relative stability of the two optical images of a chiral molecule. Pioneering work of Rein [17] analyzed the source for the energy difference between optical antipodes that could be ascribed to parity nonconservation [18]. A theoretical procedure, and an uncoupled Hartree-Fock (UCHF) algorithm for quantitative estimates [19,20], were widely applied by Mason and Tranter [21–24]. In the light of the results obtained later on via other approaches, these earlier attempts appear to underestimate the parity-violating energy difference between two mirror image molecules by one order of magnitude [25–31]. Fully relativistic methods have also been employed to calculate *P*-odd energy contributions in CHFClBr [32] and in  $H_2X_2$  ( $X=O, S, Se, Te,$  and  $Po$ ) molecules [33].

The theoretical estimates of parity-violating energies in enantiomeric molecules hitherto obtained seem to provide a quite limited statistics in agreement with phenomenology: naturally occurring *L*- $\alpha$ -amino acids [23,27], *D*-sugar precursor hydrated *D* glyceraldehyde [30], and *d* camphor [31] are predicted to be more stable than their optical antipodes not found in nature, but the calculated parity-violating energy differences (PVED), approximately  $10^{-19}$  hartree, are so small that one cannot really speak of thermodynamic stabilization of one enantiomer over the other. In any event, the idea that even such small energy differences might be effective, and sufficiently large to cause chiral discrimination, has been put forward by many scientists.

It has long been known that optically inactive reagents cannot give rise to asymmetric syntheses in conditions of near equilibrium, but stereoselection might take place in the transient states of a kinetic process, triggered by a small fluctuation, or any suitable perturbation. Further development of the system could be conditioned by feedback, e.g., an autocatalytic step preferentially generating the same enan-

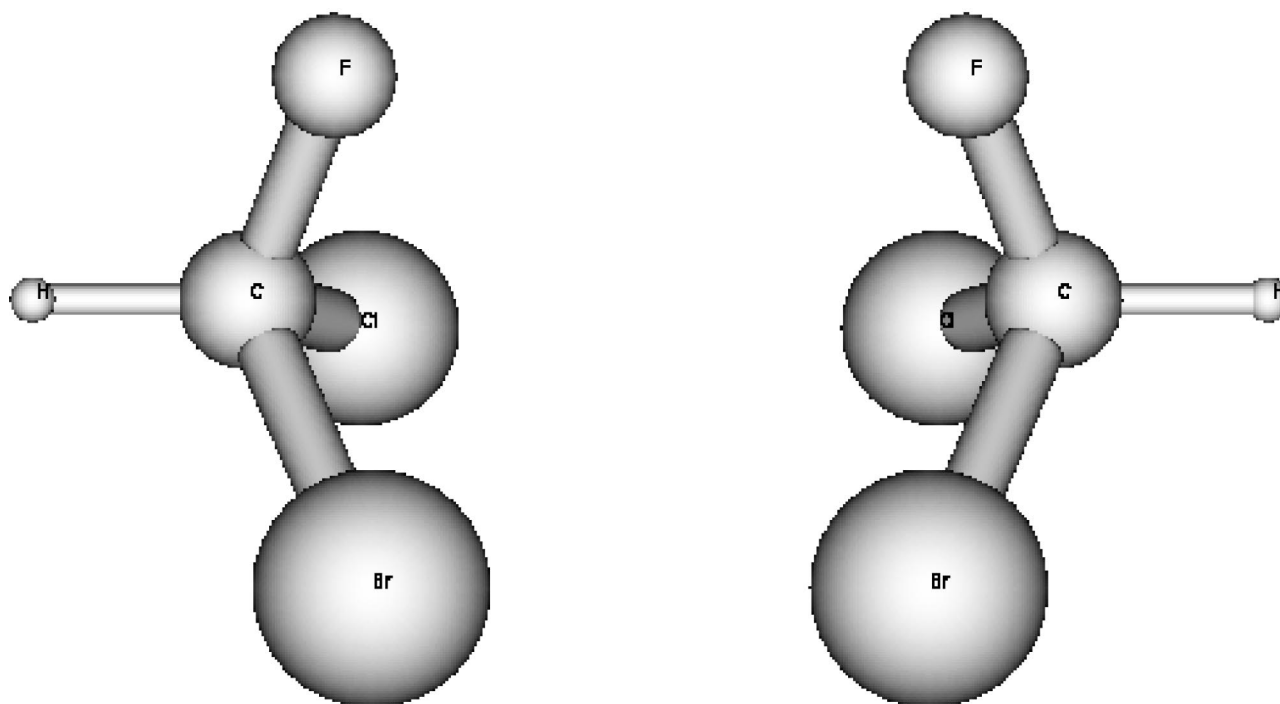


FIG. 1. The *S* and *R* enantiomers of the CHFClBr molecule.

tiomer and inhibiting formation of the antagonist species. From the mathematical point of view, the nonlinear dynamical system describing the flow, i.e., a set of differential equations depending on some parameters, would pass through a bifurcation point [34], leading to two unevenly probable branching routes: only one is therefore preferred by the system.

According to these basic ideas, a number of more or less plausible hypotheses have been formulated to rationalize homochirality in our planet. An “accumulation principle” has been advocated by Yamagata to explain the destruction of the “imaginary” left-handed form of DNA induced by the asymmetry of electromagnetic radiation [35]. A general dynamical model of far-from-equilibrium processes was early formulated by Frank [36]; Seeling [37,38], and Decker [39,40] put forward models of multistationary state kinetics whereby stable asymmetric configurations are arrived at. A widely cited reliable symmetry-breaking catastrophic bifurcation scheme in the spirit of Frank’s [36] has been reported by Kondepudi and Nelson [41–44]. A paper describing a very similar method had been published by Vitagliano and Vitagliano in 1976 [45]. Asymmetric autocatalysis can lead to the excess of one enantiomeric species according to Soai *et al.* [46].

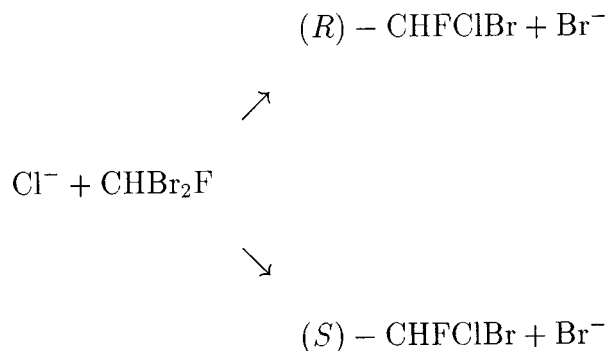
Strong criticism of straightforward applications of kinetic models, introducing weak asymmetric advantage factors in noncooperative, as well as cooperative systems, had been expressed, however, by Avetisov *et al.* [47]. Very recently, the importance of cooperative effects in solution has been reexamined [48,49]. Amplification mechanisms that can occur during the crystallization of optical isomers have been discussed by Keszthely [50] and Szabó-Nagy and Keszthely [10]; Tennakone examined a mathematical model to justify the enantioselection due to weak neutral currents [51]; a generalized Frank model was outlined by Gutman *et al.* [52].

A rather different approach was put forward by Abdus Salam, who, admitting the special role of the  $Z^0$  interaction, speculated on quantum-mechanical cooperative and condensation phenomena, which could give rise to a second-order phase transition, including *D* to *L* transitions, below a critical temperature, and suggested the possibility that life might have evolved on the Earth [18].

### III. STUDY OF A CHEMICAL REACTION PRODUCING CHFClBr

In a first attempt to gauge the role of *P*-odd effects in a kinetic process, Tranter had evaluated the parity-violating energy contributions along a chemical reaction yielding *L*- $\alpha$ -aminopropionitrile [24]. A prebiotic process involving this molecule might lead to a possible precursor of the amino acid alanine. A number of simplifying assumptions were retained by him to make the calculations feasible. However, for many reasons, it is preferable to start from some simpler dynamic system with a minimal set of initial conditions, in order to make an assessment of the hypothesis that kinetic, rather than thermodynamic effects are possibly responsible for homochirality.

The bimolecular  $S_N2$  nucleophilic reaction



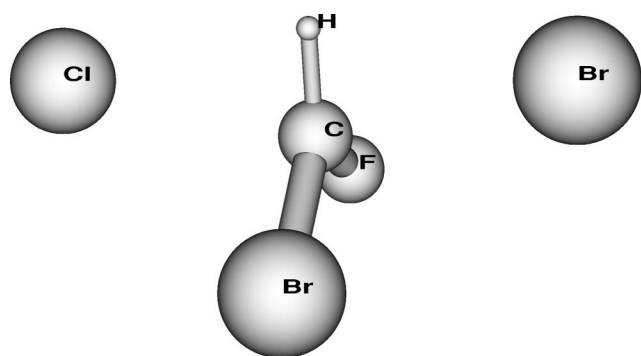


FIG. 2. The activated complex in the transition state of the chemical reaction  $\text{Cl}^- + \text{HCBBr}_2\text{F} \rightarrow (S)\text{-HCBBrClF} + \text{Br}^-$ .

producing a racemic mixture of (*S*)- and (*R*)-CHFCIBr, see Fig. 1, has been investigated in this work, which is aimed at obtaining some preliminary, but reliable, information on the role of electroweak forces influencing a kinetic process that starts from achiral reagents and can eventually yield two alternative enantiomeric products. Every step of the reaction is necessarily governed by energetic factors, corresponding to an extremum path over an energy hypersurface.

The step relative to a critical decision that the evolving system makes is encountered in the vicinity of the transition point, where the minor energy route leading to the products is chosen. Consequently the energy difference between transition states of opposite chirality should be an additional indicator of the direction preferred by an asymmetric chemical reaction, reasonably more suitable than the mere PVED separating the two possible final enantiomeric products.

In this reaction an incoming nucleophilic  $\text{Cl}^-$  anion displaces a bromine atom bonded to the carbon atom in a  $\text{CHFBr}_2$  reactant: the quasitrahedral bond structure about the carbon nucleus starts breaking, an umbrella inversion occurs, and the dynamical system passes through the transition state represented in Fig. 2, where three quasiplanar CH, CF, and CBr bonds are found. The CCl and CBr bonds lie in two directions almost perpendicular to the others.

It should be observed that the six-atom activated complex  $\text{CHFCIBr}_2^-$  is a chiral species not superimposable to its mirror image. As the reaction goes on, the activated complex expels a bromine anion, eventually producing the stable product CHFCIBr. The typical quasitrahedral bond arrangement about the asymmetric carbon nucleus, lost in the transition state, is recovered.

The geometrical parameters, bond distances, and bond angles have been evaluated via the GAMESS program [53] for the activated complex; the 6-31g basis set [54] has been adopted in the geometry optimization.

The configuration of the transition state corresponds to one negative eigenvalue of the Hessian, i.e., the second derivative matrix, in a saddle point of the unperturbed electronic potential-energy surface (PES), connecting two local valleys [55]. By definition such a point is nonstable. The nuclear coordinates of the activated complex and of the final stable product (*S*)-CHFCIBr are reported in Tables I and II, respectively.

References [56,57] provide a comparison between theo-

TABLE I. The internal coordinates of the chiral complex in the transition state of the  $\text{SN}_2$  reaction  $\text{Cl}^- + \text{HCBBr}_2\text{F} \rightarrow (S)\text{-HCBBrClF} + \text{Br}^-$  via restricted Hartree-fock (RHF) 6-31g optimization; see the text.

Bond distances (Å)	
H-C	1.053
Cl-C	2.476
Br1-C	1.889
F-C	1.324
Br2-C	2.617
Bond angles	
Cl-C-H	78.644°
Br1-C-H	123.718°
F-C-H	120.880°
Br2-C-H	77.598°
Dihedral angles	
Br1-C-H-Cl	91.476°
F-C-H-Cl	88.744°
Br2-C-H-Cl	177.342°

retical and corresponding experimental structural data for CHFCIBr; the absolute configuration of bromochlorofluoromethane has been assigned via theoretical and experimental criteria [58]. The nuclear coordinates reported in Tables I and II have been employed in the calculation of the parity-violating energies. The theoretical approach outlined in previous references [26,27,30,31] has been applied to calculate the parity-violating energy shift (PVES) in the attempt to test the hypothesis that a  $\text{SN}_2$  reaction is biased by electroweak forces.

Three main features need to be borne in mind to characterize the limits of the preliminar results arrived at in this paper: (i) The self-consistent-field approach retained in the calculation is basically unsuitable to describe molecular dissociation quantitatively. Theoretical procedures taking into account the effects of electron correlation should be applied to obtain more accurate structural parameters for the acti-

TABLE II. Internal coordinates of (*S*)-CHFCIBr via rhf 6-31g(*p,d*) optimization; see the text.

Bond distances (Å)	
H-C	1.074
Cl-C	1.750
Br-C	1.941
F-C	1.328
Bond angles	
Cl-C-H	108.7°
Br-C-H	107.5°
F-C-H	109.9°
Dihedral angles	
Br-C-H-Cl	-121.8°
F-C-H-Cl	119.6°

TABLE III. The SCF energy  $E_{\text{scf}}$  (hartree) and the CHF parity-violating energy shift ( $E_{\text{pv}} \times 10^{-20}$  hartree) of the chiral transition state of the  $\text{SN}_2$  reaction and of the final product ( $S$ )- $\text{CHBrClF}$  in its ground state.

	$E_{\text{scf}}$	$E_{\text{pv}}$
Transition state	-5741.083497	-1126.68
Ground state	-3169.184947	-465.23

vated complex. (ii) Owing to the limited capabilities of the computer programs developed by us so far, the second-order perturbed approach used to estimate the parity-violating energy shift does not take into account two-electron contributions to the spin-orbit Hamiltonian, which are known to be sizable [59,60,33,61]. In any event, to preserve the full *ab initio* character of the present calculation, we did not consider the possibility of phenomenological shielding corrections to the spin-orbit one-electron term. (iii) Electron correlation effects on the parity-nonconserving energy were neglected.

The primitive basis set adopted in this study has been previously used to estimate the vibrational frequency shifts between the  $\text{CHFClBr}$  enantiomers due to weak neutral currents [62]: it consists of a (primitive)  $\rightarrow$  [contracted] set of Gaussian functions:  $(5s) \rightarrow [3s]$  on H, and  $(9s5p) \rightarrow [5s3p]$  on C and F from van Duijneveldt [63],  $(13s10p) \rightarrow [8s6p]$  on Cl from McLean and Chandler [64], and  $(16s12p5d) \rightarrow [11s10p4d]$  on Br from Werner and Rosmus [65].

The calculations indicate that the  $S$ -enantiomer of  $\text{CHFClBr}$  is more stable than the  $R$  enantiomer due to parity-violating effects; see Table III. The energy difference between them is  $0.93046 \times 10^{-17}$  hartree for the geometry adopted in the calculation. The chiral activated complex that is found in the transition state leading to the  $S$  enantiomer is more stable, by  $2.2543 \times 10^{-17}$  hartree, than its mirror image; see Table IV. These values are a few orders of magnitude larger than those previously estimated for other chiral molecules [22,23,26,27,30,31,28], which confirms that  $\text{CHFClBr}$  is a suitable candidate for detecting the effects of electroweak forces.

As the extremum points of the parity-conserving  $E_{\text{scf}}$  energy and of the  $E_{\text{pv}}$  energy surfaces do not evidently coincide, the latter has been analyzed also in the proximity of the transition point. It is interesting to observe, see Table IV, that the  $P$ -odd energy smoothly increases, in absolute value, in the portion of the reaction path lying beyond the saddle transition point of the  $E_{\text{scf}}$  hypersurface, and descending toward the ( $S$ )- $\text{CHFClBr}$  product. For a number of points corresponding to the progressive detachment of the  $\text{Br}^-$  and bonding of  $\text{Cl}^-$ , a steep enhancement of the parity-violating energy was found.

#### IV. CONCLUSIONS

The results obtained in the present study suggest that electroweak forces may influence a chemical dynamical system.

TABLE IV. Parity violation energies  $E_{\text{pv}} \times 10^{20}$  hartree corresponding to different values of C-Cl and C-Br bond distances along the reaction path  $\text{Cl}^- + \text{CHBr}_2\text{F}$ .

$R_{\text{C-Cl}}$	$R_{\text{C-Br}}$	$E_{\text{SCF}}$	$E_{\text{pv}}$
2.4282	2.6598	-5741.0842	-2038
2.4122	2.6743	-5741.0847	-2477
2.3958	2.6885	-5741.0852	-2690
2.3794	2.7029	-5741.0858	-3043
2.3629	2.7170	-5741.0855	-3255

The analysis of a  $\text{SN}_2$  reaction producing  $\text{CHFClBr}$  shows that a chiral transition state is energetically stabilized by parity-violating effects. The extent of such a stabilization is much larger than that of the final reaction product, ( $S$ )- $\text{CHFClBr}$ . The PVEDs separating the enantiomeric transition states and the final products, according to the theoretical determinations carried out in this work, are so small that very little deviations from the 50%–50% racemic mixture of ( $S$ )- $\text{CHFClBr}$  and ( $R$ )- $\text{CHFClBr}$  can be expected. Even if such a tiny imbalance might be significant in the light of the approaches mentioned in Sec. II, experimentally detectable effects could be sought in chemical reactions involving heavier atoms, e.g., the synthesis of  $\text{CHFClI}$ , owing to the well-known dependence of  $P$ -odd energy on the fifth power of the atomic number [20].

Although the limitations (i)–(iii) discussed in Sec. III imply that really accurate numerical estimates would demand future extended work, we believe that the preliminary test performed in this paper proves the reliability of the idea that kinetic, rather than thermodynamic, effects should probably be advocated to explain homochirality. In other words, the mere energy difference separating two isolated enantiomers may be too small to explain the preponderance of only one of them. Instead, all the intermediate steps of the dynamic process yielding preferably one chiral form seem to be actually driven by electroweak forces. In a chemical reaction like the one studied in this work, every point on the path along the energy hypersurface which describes the evolution of the system between two local minima, corresponding to the reactants and the products, is effectively biased by parity-violating mechanisms. The saddle point, corresponding to the enantiomeric transition state of the process, can be crucial in determining the evolution of the dynamical system towards one enantiomer.

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