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Theoretical determination of parity-violating vibrational frequency differences between the enantiomers of the CHFClBr molecule

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A coupled Hartree-Fock procedure has been employed to estimate the frequency shift in the infrared spectra of the *S* and *R* enantiomers of the CHFClBr molecule due to the parity-violating electroweak interaction. The calculations indicate that a resolving power $\nu/\Delta\nu \approx 1\times10^{16}$, i.e., three orders of magnitude larger than that obtained in recent experiments, would be necessary to detect the parity-violating effects. The largest frequency shift was found for C-Cl stretching.

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I. INTRODUCTION

The violation of space-inversion symmetry at the elementary particle level was experimentally demonstrated by Chieng-Shiung Wu and her colleagues in 1957 [1], shortly after the theoretical report by Lee and Yang [2]. The weak force carried by the massive charged bosons $W^{\pm}$, responsible for the β decay of radionuclides, provides a paradigm of parity-violating effects: the asymmetry experimentally observed in the decay of ^{60}Co into ^{60}Ni [1] proved that the emitted electrons have negative helicity, i.e., they are predominantly polarized in the opposite direction to their motion in space.

At the atomic level, it was recognized early that a unified electroweak theory leads to nonconservation of parity [3–5]. Accurate measurements in atoms furnished crucial tests for the standard model at low energy [6,7]. The absence of reflection symmetry in atoms was demonstrated [8] by the rotation of plane-polarized light passing through heavy atom gases. A different manifestation of parity nonconservation in atoms has been observed in cesium, and a measurement of the nuclear anapole moment has recently been reported [9].

In spite of these successful findings, no definitive proof has yet been produced that the effects of parity-violating forces are detectable in molecules. This question is very important and timely for many reasons. To begin with, the hypothesis that a chiral force is operating in the universe, causing the chemistry of life to prefer handedness [10], is nowadays the object of widespread discussion. If this were proved, Pasteur's grand conjecture [10], ''L'univers est dyssimétrique,'' would also justify a physical foundation of biochemistry in terms of electroweak forces.

How to solve the problem of the origin of enantioselection in terrestrial living organisms is still matter for lively debate. Life is characterized by homochirality of organic molecules: only L-α-amino acids and D-sugars are present in plants and animals of our planet, whereas racemic mixtures of chiral species are usually produced via abiotic syntheses in chemical laboratories. The idea that parity-violating neutral currents mediated by the Z^0 boson and acting at the molecular level can be the cause of homochirality was formulated by Rein [11]: an energy difference, and a corresponding different stability, between optical isomers could be ascribed to this effect.

Experimental evidence that the manifestation of weak neutral currents can be observed in molecules has long been sought for an overall assessment of these hypotheses. Barra and Robert suggested that a difference between the chemical shifts of the same nucleus belonging to different optical antipods can be detected via NMR spectroscopy [12]. Letokhov made the proposal that the signature of weak interactions can be discovered as the difference of vibrational frequencies between the enantiomers of the same chiral molecule [13]. Another suggestion has been made by Quack [14]. Arimondo *et al.* compared the rovibrational transitions in the separated isomers of *d* and *l*-camphor by measuring the inverted Lamb dips. They established an upper bound of 300 kHz (corresponding to a relative accuracy $\Delta\nu/\nu = 1\times10^{-8}$) for the frequency shift between the optical isomers [15].

Bromochlorofluoromethane (CHFClBr) was early proposed as an ideal candidate for a beat note experiment between two lasers locked on the infrared absorption line of its enantiomers [16]. The physical and chemical properties of this molecule have been very well studied. An experimental determinations of its absolute configuration [17] as well as precise spectroscopic parameters [18–20] have been reported.

More recently a major step forward has been made in laser technology: a crucial experiment is presently in progress where saturation spectroscopy is employed to gauge the role of electroweak forces in molecular physics, via a direct comparison of the rovibrational transitions of the enantiomers of CHFClBr in the 9.3 μm spectral region [21–23]. The gain of sensitivity ($\Delta\nu/\nu = 4.10\times10^{-13}$) with respect to Ref. [15] is approximately five orders of magnitude. The frequencies of the saturation resonances of the enantiomers were found to be the same within the uncertainty of 13 Hz [21–23]: if there is any effect due to electroweak interaction, it is smaller than this bound. A theoretical estimate of the frequency shifts in the vibrational bands of CHFClBr is therefore opportune, as it could provide information on (i)

TABLE I. Vibrational frequencies, IR intensities, and parity-violating vibrational frequency shifts (in Hz/10^{-4}) for each normal mode Q of the S enantiomer of the CHBrClF molecule.

Q	BLQ[a]		I/I[b]			II/I[c]			III/III[d]			
	$\overline{\nu}_0$	G	$\overline{\nu}_0$	IR int.	Shift	$\overline{\nu}_0$	IR int.	Shift	$\overline{\nu}_0$	IR int.	Shift	
1	223.6	0.0018	233.4	0.009	0.458	243.4	0.001		242.16	0.0016	0.14	
2	313.0	0.0051	331.1	0.051	−0.103	348.6	0.007		346.61	0.0058	1.84	
3	425.2	0.020	427.0	0.045	−4.75	465.6	0.027		462.78	0.0025	−4.95	
4	663.6	1.31	697.5	0.870	3.01	722.8	1.075	−3.69	719.92	1.1633	−2.55	C-Br stretching
5	787.0	3.78	824.8	5.167	13.6	875.3	4.645	18.6	858.36	5.3206	18.08	C-Cl stretching
6	1077.2	2.59	1122.5	4.109	−7.31	1229.7	4.613	−8.83	1235.16	5.0797	−7.26	C-F stretching
7	1202.8	0.79	1349.2	2.358	−3.43	1362.0	1.996		1354.98	2.5787	−6.86	C-H bending
8	1306.2	0.142	1440.2	0.566	−9.18	1465.3	0.415		1481.83	0.6215	−11.02	C-H bending
9	3025.5	0.0045	3356.3	0.002	2.11	3367.7	0.028	1.12	3345.89	0.0344	1.50	C-H stretching

[a] Experimental results from Ref. [18]; frequencies $\overline{\nu}_0$ are in cm^{-1} and absolute band strenghts G in pm^2.

[b] Equilibrium geometry, vibrational frequencies, and IR intensities (in D^2 amu^{-1} Å^{-2}) calculated at SCF level of theory with the GAMESS package [38] adopting basis set I; parity-violating vibrational frequency shifts calculated with the SYSMO package [31] within the CHF approach using basis set I.

[c] Equilibrium geometry, vibrational frequencies, and IR intensities (in D^2 amu^{-1} Å^{-2}) calculated at SCF level of theory with the GAMESS package [38], adopting basis set II; parity-violating vibrational frequency shifts calculated with the SYSMO package [31] within the CHF approach using basis set I.

[d] Equilibrium geometry, vibrational frequencies, and IR intensities (in D^2 amu^{-1} Å^{-2}) calculated at SCF level of theory with the GAMESS package [38], adopting basis set III; parity-violating vibrational frequency shifts calculated with the SYSMO package [31] within the CHF approach using basis set III.

the magnitude of the effect and (ii) the spectral regions where it is expected to take place to higher extent, corresponding to a larger bias of a given normal mode by weak currents.

II. THEORETICAL CALCULATION

A simple uncoupled Hartree-Fock (UCHF) computational scheme for evaluating the contribution to the electronic energy of a molecule arising from weak forces has been presented by Rein *et al.* [24,25] and widely employed by Mason and Tranter [26,27]. Perturbed coupled Hartree-Fock (CHF) procedures, equivalent to the random-phase approximation (RPA), were shown to provide more accurate theoretical estimates of the parity-violating energy contributions in molecules [28–31]. The CHF approach is also more reliable than the Tamm-Dancoff approximation [28], equivalent to the configuration interaction single-excitation restricted Hartree-Fock scheme (CIS-RHF) [32–34]. In any event, CHF-RPA and CIS-RHF procedures yield estimates of the parity-violating energy shift that are one order of magnitude larger than that from UCHF calculation. Accordingly, the CHF scheme described in Refs. [28–31] has been employed in extended calculations of the infrared frequency differences between the enantiomers of CHFClBr.

Allowing for the harmonic approximation, the vibrational frequencies of a nonlinear molecule with N nuclei are evaluated assuming a truncated Taylor series expression for the energy,

$$E=E_e+\frac{1}{2}\sum_{i=1}^{3N-6}\lambda_i Q_i^2,\quad \lambda_i=\frac{\partial^2 E}{\partial Q_i^2},\tag{1}$$

where E_e is the energy at equilibrium geometry, Q_i are normal coordinates corresponding to $3N-6$ modes, and the force constants are related to the vibrational frequencies

$$\nu_i=\frac{\lambda_i^{1/2}}{2\pi}.\tag{2}$$

The total energy E of the molecule is the sum of the parity-conserving electronic term E_{pc} and a parity-violating term E_{pv}, so that

$$\frac{\partial^2 E}{\partial Q_i^2}=\frac{\partial^2 E_{pc}}{\partial Q_i^2}+\frac{\partial^2 E_{pv}}{\partial Q_i^2}=\lambda_{i,pc}+\lambda_{i,pv}.\tag{3}$$

Accordingly, the vibrational frequency shift caused by the parity-violating interaction is

$$\Delta\nu_i=\frac{(\lambda_{i,pc}+\lambda_{i,pv})^{1/2}-\lambda_{i,pc}^{1/2}}{2\pi}\approx\frac{\lambda_{i,pv}}{4\pi\lambda_{i,pc}^{1/2}}.\tag{4}$$

This quantity changes sign on passing from one enantiomer to the other; therefore the frequency difference between them equals $2\Delta\nu_i$.

Employing the computational technique previously outlined in Refs. [28–31] and adopting the same notation, the electroweak contribution to the energy is a second-order cross term

$$E_{pv,so}=-\frac{1}{\hbar}\sum_{j\neq a}\frac{2}{\omega_{ja}}\mathrm{Re}(\langle a|H_{pv}|j\rangle\langle j|H_{so}|a\rangle)\tag{5}$$

between the Bouchiat Hamiltonian [3–5]

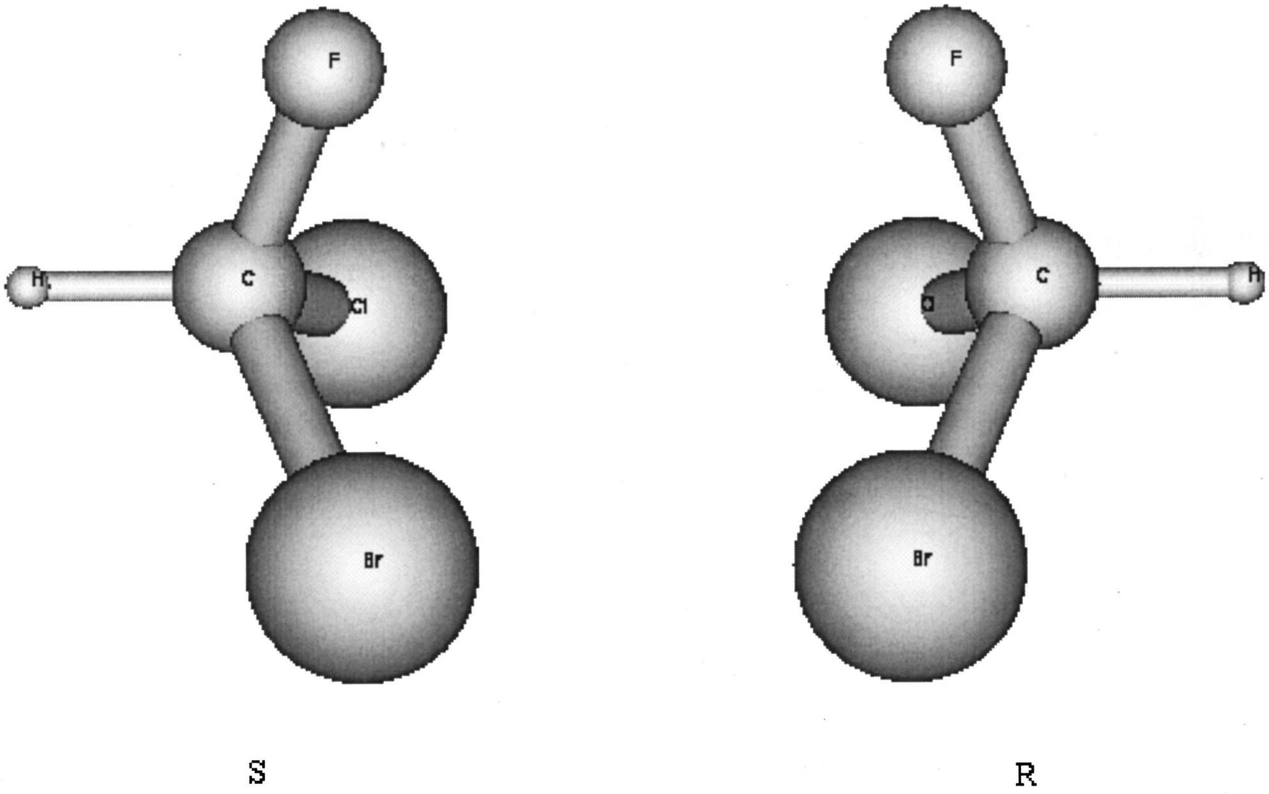

FIG. 1. The *S* and *R* enantiomers of the CHFClBr molecule.

$$H_{pv}=-\frac{\Gamma}{2}\sum_{I=1}^{N}\sum_{i=1}^{n} Q_I\{\mathbf{p}_i\cdot\boldsymbol{\sigma}_i\,,\delta(\mathbf{r}_i-\mathbf{R}_I)\}_+ \qquad (6)$$

and the one-electron spin-orbit Hamiltonian

$$H_{so}=\frac{\beta^2}{\hbar}\sum_{I=1}^{N}\sum_{i=1}^{n} Z_I|\mathbf{r}_i-\mathbf{R}_I|^{-3}\boldsymbol{\sigma}_i\cdot(\mathbf{r}_i-\mathbf{R}_I)\times\mathbf{p}_i\,. \qquad (7)$$

The contribution of two-electron terms to the spin-orbit interaction could not be calculated due to the limited capabilities of the computer programs developed by us so far. According to some suggestions, they should be included in accurate evaluations of the total parity-violating energy in small molecules [35,34].

As we are at present essentially interested in estimating the order of magnitude of the frequency shift (4) in the infrared spectral range that can most profitably be investigated by spectroscopists in the very near future, the evaluation of the two-electron contributions is the object of investigations in progress. In any event, the explicit calculation of the spin-orbit interaction term is necessary only within a nonrelativistic computational approach: if four-component Dirac-Hartree-Fock wave functions are employed, the parity-violating energy contribution is obtained as an expectation value of the γ_5 Dirac matrix, according to the procedure reported by Quiney *et al.* [36,37]. Such an approach is possibly more practical than the nonrelativistic one in some cases.

Three large Gaussian basis sets have been employed to evaluate the equilibrium geometry, the normal modes, the vibrational frequencies, and the corresponding absorption intensities at the self-consistent field (SCF) level of theory with the GAMESS package [38], in the attempt to test the stability of the theoretical predictions. Basis set I consists of a (primitive) → [contracted] set of Gaussian functions: $(5s)\rightarrow[3s]$ on H and $(9s5p)\rightarrow[5s3p]$ on C and F from van Duijneveldt [39], $(13s10p)\rightarrow[8s6p]$ on Cl from McLean and Chandler [40], and $(16s12p5d)\rightarrow[11s10p4d]$ on Br from Werner and Rosmus [41]. Basis set II is a double-zeta basis set, plus three polarization functions on all atoms but Br, from the compilation by Dunning and Hay [42], i.e., $(3s3p)\rightarrow[2s3p]$ on H, $(9s5p3d)\rightarrow[3s2p3d]$ on C and F, $(11s7p3d)\rightarrow[6s4p3d]$ on Cl, and $(14s11p8d)\rightarrow[6s4p4d]$ on Br. Basis set III contains the Gaussian functions of basis set I left uncontracted, with the addition of polarization functions on all atoms, i.e., $(5s1p)\rightarrow[5s1p]$ on H and $(9s5p1d)\rightarrow[9s5p1d]$ on C and F (for the polarization functions see Ref. [43]), $(12s9p2d)\rightarrow[12s9p2d]$ on Cl with polarization functions from Refs. [44], and $(16s12p5d1f)\rightarrow[16s12p5d1f]$ on Br with polarization function from Refs. [45,46], for a total of 211 Gaussian-type orbitals.

Basis sets I and III have also been used to compute the parity-violating energy with the SYSMO package [31]; in particular, we have considered three combinations of basis sets, hereafter referred to as I/I, II/I, and III/III (see Table I). The entry on the left of a slash specifies the basis set used for the geometry search plus Hessian calculations, that on the right indicates the basis set adopted for determination of parity-violating energy. All calculations overestimate the IR absorption frequencies, which is a well known drawback of the SCF approach. The discrepancies between theoretical and experimental data are smaller for basis set I (see Table I), which, however, should be considered fortuitous. The values of calculated and experimental intensities show similar trends.

The calculations indicate that the *S* enantiomer of CHFClBr (see Fig. 1) is more stable than the *R* enantiomer due to parity-violating effects. The energy difference between them is $2|E_{pv}|=1.1264\times10^{-17}$, $0.968\,65\times10^{-17}$, and $0.726\,88\times10^{-17}$ hartree, respectively, for the calculations I/I, II/I, and III/III, at their equilibrium geometries. These values are a few orders of magnitude larger than those previously estimated for other chiral molecules [26–32] which confirms that CHFClBr is a more suitable candidate for detecting the effects of electroweak forces.

A pointwise procedure has been adopted to evaluate the Hessian matrix of the parity-violating energy hypersurface and the frequency shifts at the equilibrium geometry of the *S* enantiomer (the sign would be reversed for the *R* enantiomer). A minimum (maximum) of seven (eleven) theoretical determinations of E_{pv}, corresponding to molecular motion along a given normal coordinate, were found necessary to obtain stable $\lambda_{i,pv}$, $i=1,\ldots,9$, values in the calculations I/I. The results from calculation II/I corresponding to normal modes 1, 2, 3, 7, and 8 are not reported in Table I as they did not stabilize. Only seven points were sufficient to obtain stable results for calculation III/III. Shifts of the same magnitude but different sign were obtained for the fourth normal mode, i.e., C-Br stretching. All estimates are numerically stable; however, owing to the better overall features of basis set III, we think that the value $\approx -3\times10^{-4}$ Hz should be more reliable. At any rate, these findings clearly indicate that the theoretical evaluation of the frequency shifts needs to be carefully performed.

As regards the other normal modes, all calculations yield quite similar results. In any event, the frequency shifts due to parity-violating interactions estimated in the present study are a few orders of magnitude smaller than the upper bound experimentally determined by Daussy *et al.* [23]. Accordingly, a resolving power $\nu/\Delta\nu\approx1\times10^{16}$, i.e., ≈ 3 orders of magnitude higher than that obtained so far, would seem to be necessary to observe frequency shifts arising from electroweak forces. The spectral regions where electroweak interaction would affect the vibrational motion of the molecule to a larger extent correspond to C-Cl and C-F bond stretching (normal modes 5 and 6) and C-H bending (normal mode 8).

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