Limit on the Parity Nonconserving Energy Difference between the Enantiomers of a Chiral Molecule by Laser Spectroscopy

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We have developed a saturation spectroscopy experiment to test the prediction that enantiomers of chiral molecules have different spectra because of the parity violation associated with neutral currents in the weak interaction between electrons and nuclei. First experimental tests have been conducted on hyperfine components of vibration-rotation transitions of CHFClBr in the 9.3 μm spectral range. The frequencies of saturation resonances of separated enantiomers have been compared and found to be identical within 13 Hz ($\Delta\nu/\nu < 4.10^{-13}$).

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Introduction and historical background.—In 1974, it was suggested that the weak neutral currents can manifest themselves in the molecules with an original and simple signature: if we consider the two mirror image enantiomers of a chiral molecule, a parity violation induced by weak interactions will appear as a difference in the electronic energies of the two species [1]. Many theoretical studies have been pursued to obtain quantitative estimates of the effect in various molecules but none of them is yet able to provide a value of the expected relative energy shift, which is estimated to be between 10^{-13} and 10^{-20}. Therefore, there is no hope, in the short term, to improve our knowledge of the weak interaction by this way. However, this remains today one of the most exciting challenges in molecular physics because it is related to the intriguing question of the origin of the symmetry breaking between right- and left-handed biomolecules [2,3]. In this context, it was of great interest to perform an experiment. After the pioneering paper of Rein [1], Letokhov [4] proposed to observe the parity violation effect in molecules as a difference in vibrational frequencies. A beat note experiment [5] was proposed between two lasers locked on a vibrational line of the enantiomers of the chiral molecule CHFClBr although, at that time, this molecule was only available as a racemic mixture. In this paper, we present the first test of parity violation in molecules with a sensitivity which reaches the range of the theoretical predictions. It has been performed with the enantiomers of CHFClBr. The unique test thus far reported with separated enantiomers (on camphor with a sensitivity of 10^{-8}) [6] was far from the predictions of the theory. Other proposals using NMR on chiral molecules in an external field have been made [7].

Theoretical background.—For nonchiral polyatomic molecules we have shown, experimentally and theoretically [8–10], that one of the two states, which differ only by their parity, does not exist because of the Pauli principle applied to identical nuclei. Thus, no strict parity degeneracy can occur even if inversion and parity violation are neglected. By contrast, chiral molecules may exist in states that differ only by their handedness or by their parity, all other quantum numbers being the same. Thanks to this unique property, a simple, in principle, spectroscopic test can reveal a parity violation without ambiguity.

For chiral molecules, we can thus consider two right- and left-image states, $|\Psi^R\rangle$ and $|\Psi^L\rangle$. If the tunneling barrier of the potential energy curve is not too high, mirror symmetry is dynamically restored by the inversion mechanism. Parity commutes with the Hamiltonian and energy eigenstates are the parity eigenstates, $|\Psi^\pm\rangle = 1/\sqrt{2}\,(|\Psi^R\rangle \pm |\Psi^L\rangle)$.

Conversely, when enantiomorphic left- and right-handed species are stable, i.e., if the potential barrier is very high, the right and left states are also energy eigenstates. Now, if parity is violated, the enantiomers cease to be images of each other in a mirror (Fig. 1). The Hamiltonian matrix will remain diagonal in the handedness-eigenstates basis but the corresponding degeneracy will be removed:

$$H_H = \begin{pmatrix} E_0 + |\Delta E^{\mathrm{PV}}| & 0 \\ 0 & E_0 - |\Delta E^{\mathrm{PV}}| \end{pmatrix}. \qquad (1)$$

The parity-violating molecular Hamiltonian, H^{PV}, has essentially the same origin as in atomic physics, although it involves a sum over the electrons i and the nuclei K [11]. However, for molecules, in the nonrelativistic limit, the first-order energy correction vanishes [12] and it is therefore necessary to invoke the spin-orbit coupling, H^{SO}, to obtain a nonzero contribution:

$$\Delta E^{\mathrm{PV}} = \sum_{n\neq 0} \frac{\langle 0^-|H^{\mathrm{PV}}|n^+\rangle\langle n^+|H^{\mathrm{SO}}|0^+\rangle}{E_0 - E_n} + \frac{\langle 0^-|H^{\mathrm{SO}}|n^-\rangle\langle n^-|H^{\mathrm{PV}}|0^+\rangle}{E_0 - E_n}. \qquad (2)$$

Taking into account the $\mathbf{Z}^3$ dependence of the parity-violating term in atomic physics, the $(\alpha\mathbf{Z})^2$ dependence of the spin-orbit term where Z represents the atomic charge, a crude estimate of the order of magnitude of ΔE^{PV} can be obtained [13]:

$$\Delta E^{\mathrm{PV}} \sim 8.5 \times 10^{-21}\, \eta \mathbf{Z}_K^3 \mathbf{Z}_{K'}^2 \text{ hartree}. \qquad (3)$$

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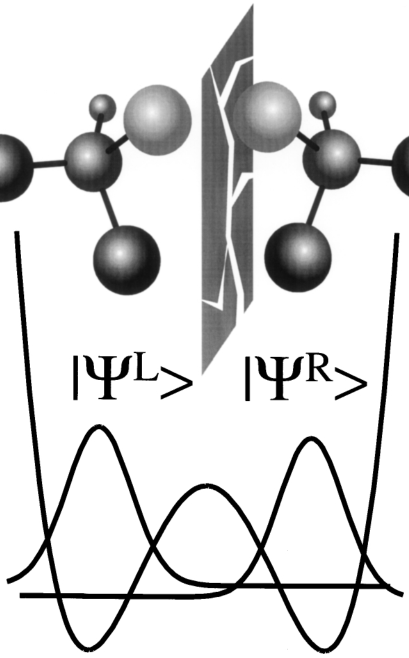

FIG. 1. Because of weak interactions, right and left enantiomers of CHFClBr are not images in a mirror.

The dominant term comes from the heaviest nuclei with the restriction that, by symmetry, the terms with $K = K'$ are negligible [14]. A multiplicative asymmetry factor η (usually $\ll 1$), which results from molecular orbital calculations, takes into account the chiral character of the molecular environment [15]. These arguments justify the choice of the molecule: we will prefer a chiral molecule with heavy nuclei located at the periphery.

Ab initio calculations have been applied to a number of molecules [16]: the L series of glycine, alanine, valine, serine, and aspartic acid; and the D-sugar series, which are actually the species existing on earth, were found to be preferentially stabilized by the electroweak interaction: $\Delta E_{\mathrm{el}}^{\mathrm{PV}} \sim (-0.84 \text{ to } -2.29) \times 10^{-20}$ a.u., which gave some credit to speculations in biochemistry. Recent calculations confirm a large enhancement (3 orders of magnitude) when carbon is replaced by sulfur [17]. In addition, the latest calculations based on more precise techniques (Coupled Hartree-Fock methods) lead to the same conclusions but with numerical results about 1 order of magnitude larger [18,19]. As another example [20], hypothetical four-atom molecules have been considered such as NFClBr, BiFClBr, and NFClAt, for which the calculated $\Delta E_{\mathrm{el}}^{\mathrm{PV}}$ are respectively 10^{-16}, 8×10^{-16}, and 10^{-13} eV, illustrating both the atomic number dependence and the role of the location of the high-Z atom.

In molecular spectroscopy, we have electronic, vibrational, or rotational degrees of freedom. Letokhov [4] suggested that, because the associated energies are proportional [21], a relative change in vibrational or rotational frequencies between right- and left-handed molecules is expected to scale with the relative change in electronic energy:

$$\frac{\Delta E_{\mathrm{el}}^{\mathrm{PV}}}{E_{\mathrm{el}}} \approx \frac{\Delta E_{\mathrm{vib}}^{\mathrm{PV}}}{E_{\mathrm{vib}}} \approx \frac{\Delta E_{\mathrm{rot}}^{\mathrm{PV}}}{E_{\mathrm{rot}}}. \tag{4}$$

This argument is in favor of performing vibrational spectroscopy which usually provides the highest relative resolution and sensitivity.

Experiment.—Today CHFClBr is one of the best test molecules since it is one of the simplest stable chiral molecules and a bromine atom with a high-Z value ($Z_{\mathrm{Br}} = 35$) is located at the molecular periphery. Another practical key point is the high-quality experimental and theoretical spectroscopic data available on CHFClBr. In particular, the strong ν_4 CF stretching fundamental band has been fully analyzed [22], which is a necessary starting point for any ultrahigh resolution experiment.

Experimental projects were held in abeyance over twenty years because the final difficulty of the resolution of CHFClBr enantiomers was solved successfully only recently [23]. The link between the conformation and the optical activity of the two isomers of CHFClBr was established even more recently by the group of Collet [24]: S-(+) and R-(−). This group has prepared for us a sample of R-CHFClBr with an enantiomeric excess (ee) of $(22 \pm 2)\%$ and a sample of S-CHFClBr with an ee of $(56,5 \pm 0,5)\%$. This has enabled us to perform the first sensitive test of parity violation in molecules.

The principle of the experiment is the following (Fig. 2): we use a CO_2 laser whose frequency is shifted by 40 MHz with an acousto-optic modulator (AOM) for optical isolation purposes. Then, a sideband generated by a 0–500 MHz tunable electro-optic modulator (EOM) is stabilized on a saturation peak detected on the transmission signal of a 1.5-m-long Fabry-Perot cavity. The frequency stabilization scheme is described elsewhere [25]. It can provide a spectral purity of 6 Hz and a long-term stability of 0.1 Hz over 100 s with an OsO_4 saturation resonance in the 10 μm spectral region. This performance is degraded by a factor of 10 with the use of one hyperfine component of the $(55, 11, 44) \leftarrow (55, 12, 43)$ rovibrational line of CHFClBr in the vicinity of the $R(14)$ CO_2 laser line of the 9.4 μm band because of the broader linewidth of the

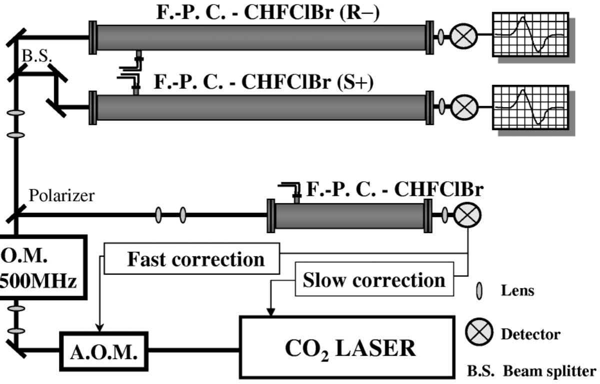

FIG. 2. Schematic diagram of the experimental setup.

reference and the reduction of the finesse of our cavity at that wavelength. However, the residual drift of the laser frequency has no impact on the sensitivity of the test.

Then, the laser carrier, shifted by the AOM, feeds twin 3-m-long Fabry-Perot cavities (7 mm waist) and the simultaneous recording of the spectra of the two enantiomers is achieved by tuning the radio frequency of the EOM. The frequency modulations required to stabilize the three resonators and to detect the molecular signals in transmission of these cavities are applied inside the laser resonator via a piezoelectric transducer, one at 41 kHz for stabilizing the optical length of the three cavities and the second at 4 kHz with a third-harmonic detection to stabilize the sideband on a molecular signal and to detect the molecular resonances of the two enantiomers. The gas pressure is 0.2 Pa and the laser power is 9 mW. The modulation parameters were optimized for the test signals and not for the stabilization. We have performed the most sensitive experiments through a study of a hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ line. The typical width of 90 kHz is due to a symmetric triplet that we can resolve in a very large cell (18 m long with an 8 cm laser beam diameter) with a linewidth of 5 kHz (Fig. 3). Actually, any difference between the two systems occurs after the beam splitter which divides the laser beam into two parts directed towards the two resonators. Most of them are compensated by the exchange of the role of the two cavities performed by filling each of them with the other enantiomer. However, this is not the case for the polarization effects and the stray fields. In fact, the lack of mirror symmetry due to some residual ellipticity ($<1\%$) of the polarization is attenuated by the finesse of the cavity. We have checked that even a circular polarization does not affect the line centers with the present sensitivity while, with a shielding of 1:1000, the effect of the earth's magnetic field is expected to be negligible.

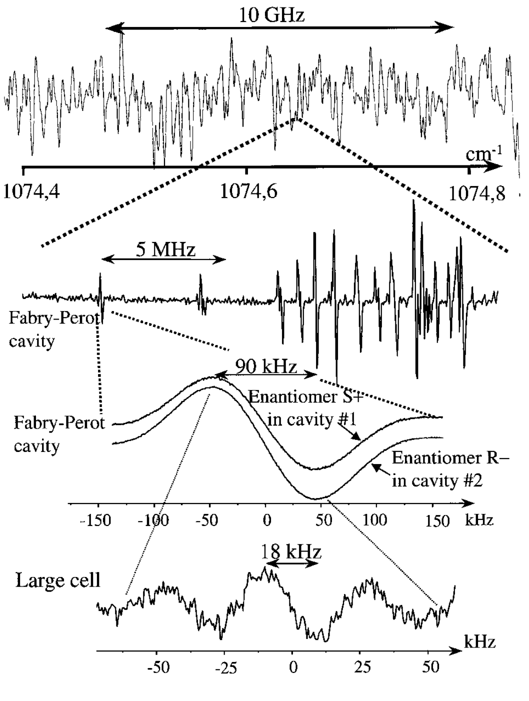

FIG. 3. ν_4 band spectra of CHFClBr at various resolutions. From top to bottom: Fourier transform spectrum (courtesy of A. Valentin—Paris VI); overview of the hyperfine structure of the $(40, 7, 34) \leftarrow (40, 8, 33)$ line; two typical spectra of the test hyperfine component recorded simultaneously; triplet substructure revealed at the highest resolution.

Results.—We have performed ten sets of measurements over ten days. For one set per day, the first half-day, each twin cavity is filled with one kind of enantiomer and, the second half-day, the enantiomers are exchanged in the cavities. When we perform an elementary measurement as described above, we obtain a systematic shift of the order of 100 Hz which is reproducible. When the role of the cavities is exchanged, we observe that the sign of the difference is changed (see Fig. 4a). This systematic effect is associated with the difference between the two systems whatever its origin. Assuming that this shift is constant over one day, we can substract it from the individual measurements (Fig. 4b). Once this compensation has been achieved, we have built the histogram from the 580 individual corrected measurements. We obtain a mean value for the frequency difference of 3, 7 Hz and a standard deviation of 47, 2 Hz, close to the uncertainties of the fits of the individual spectra (Fig. 4c).

The statistical uncertainty of this set of measurements is given by the standard deviation of this histogram divided by the square root of the number of measurements, i.e., 2 Hz. However, the systematic effects cannot be perfectly compensated and their residuals must be taken into account although we could not detect them.

We estimate that these residual systematic effects are of the order of 5 Hz, i.e., 1 order of magnitude less than the width of the histogram for two reasons: this histogram presents a nice Gaussian shape and we have checked that the data points of Fig. 4b exhibit a white distribution. Thus, the frequency difference for the resonances associated to the two samples is

$$\Delta\nu = 3,7 \pm 2 \pm 5 \text{ Hz}.$$

In addition, we have to take into account the enantiomeric excesses of the samples. We finally obtain the first measurement for the frequency difference between resonances of the two enantiomers of CHFClBr:

$$\nu(R-) - \nu(S+) = 9,4 \pm 5,1 \pm 12,7 \text{ Hz}.$$

The result of the test is, thus, negative. It gives an upper bound of $\Delta\nu/\nu \simeq 3,9 \times 10^{-13}$ for the parity violation effect.

Conclusion.—The sensitivity of this experiment is about 5 orders of magnitude higher than the previous test on camphor. This experiment is still to be considered as a preliminary test. In the short term, higher finesse resonators might be employed and samples with higher enantiomorphic excess (50% and 72%) will soon be available from Collet. A better choice of the test line should

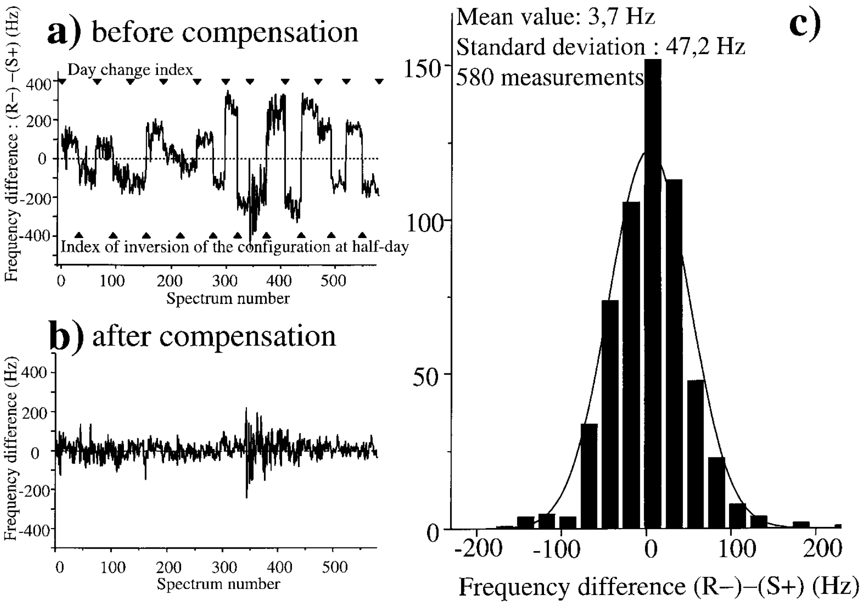

FIG. 4. (a) The measurements reveal systematic shifts induced by the differences between the cavities. (b) Compensation of systematic errors by exchange of the roles of the two cavities. (c) Histogram of the measured frequency differences for 580 measurements.

be made as we have discovered that the chosen line was a crossover resonance, sensitive to light shifts. Subsequently, higher resolution using beams of larger diameter, slow molecule detection [26], or saturation spectroscopy in molecular beams to avoid collisional shifts must be considered. Molecules with heavier atoms, such as CHFClI in which we have already observed saturation resonances, and transitions more sensitive to weak interactions, e.g., CBr or CI vibrations, must be explored. Finally, it is clear that the theory is insufficiently developed to obtain reliable estimates of the expected effects in various molecules and has to be improved substantially in order to guide further experimental developments.

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