

Improved sensitivity in the search for a parity-violating energy difference in the vibrational spectrum of the enantiomers of CHFCIBr

M. Ziskind, C. Daussy, T. Marrel, and Ch. Chardonnet^a

Laboratoire de Physique des Lasers^b, Université Paris 13, 99 avenue J.-B. Clément, 93430 Villetaneuse, France

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Abstract. The theoretical prediction that enantiomers of chiral molecules have different spectra because of parity violation associated with neutral currents in the weak interaction has been experimentally looked for. Last searches of a frequency difference in the vibrational spectrum of the enantiomers of CHFCIBr obtained with our infrared saturation spectrometer is presented. The frequencies of a saturation resonance of separated enantiomers of CHFCIBr have been compared at a 5×10^{-14} level. A residual pressure shift probably induced by uncontrolled impurities of the samples has been observed and found to limit our experimental sensitivity. Finally no parity violating frequency difference is observed within the present sensitivity of 2.5×10^{-13} . A new experimental scheme is proposed which should let the parity violation effect observable.

PACS. 33.15.Bh General molecular conformation and symmetry; stereochemistry – 11.30.Er Charge conjugation, parity, time reversal, and other discrete symmetries – 33.20.Ea Infrared spectra

1 Introduction

The weak interaction is the only fundamental interaction which does not respect left-right symmetry. This has been observed in 1957 in the famous experiment of β^- disintegration of the Co nucleus [1]. Thanks to the Z^0 boson which is the neutral vector of the weak interaction, it has been suggested that parity violation could show up with stable atoms [2]. Although this interaction is of extreme short range, after the first observation, several precise atomic experiments were achieved and confirmed the standard model to a high accuracy [3,4]. In 1974, it was suggested that parity violation can manifest itself in the molecules with an original and simple signature: if we consider the two “mirror image” enantiomers of a chiral molecule (Fig. 1), left-right symmetry breaking will appear as an electronic energy difference between the two species [5]. Considering the weakness of the effects, it is broadly admitted that the weak interaction may be neglected in molecular physics and even more clearly in chemistry and biology. However, it is remarkable that nature, on earth, has performed marked choices between right and left. The most well-known example is the right-handed double helix of the DNA molecule. The origin of homochirality emergence in biomolecules, and the possible role of weak interaction, is the subject of several contro-

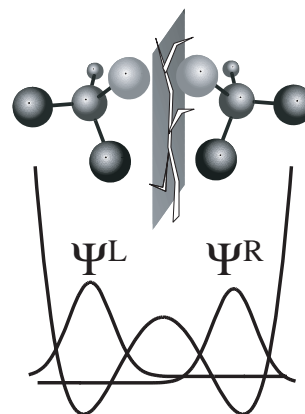


Fig. 1. Enantiomers of a chiral molecule are image each other in a mirror except if there is parity violation.

versial conjectures [6,7]. This is meaningful only if the production in excess of the more stable molecule is larger than the unavoidable random fluctuations. This is why models of molecular dynamics establish a relation between the energy difference, the size of the sample and the time required for a complete selection of one species over the other [8]. This is one motivation of looking for a parity violation effect in molecules, which has never been observed so far.

^a e-mail: chardonnet@galilee.univ-paris13.fr

^b UMR 7538 du CNRS

In 1998 we performed a first attempt to observe a parity violation effect on separated enantiomers of a chiral molecule. We looked for a difference in the vibrational spectrum of the two enantiomers of CHFCIBr which is one of the simplest chiral molecules. No effect has been observed and we could give an upper bound of $\Delta\nu/\nu = 3.9 \times 10^{-13}$ for the parity violation effect [9]. After a brief outline of the general theoretical and experimental background we will present our last attempt to observe a parity violation effect with our infrared saturation spectrometer on new molecular samples.

1.1 Theoretical basis

For a chiral molecule, we can consider two right- and left-handed states $|\Psi^R\rangle$ and $|\Psi^L\rangle$. If a molecule can change its configuration by tunnel effect, mirror symmetry is dynamically restored and energy eigenstates are the parity eigenstates, $|\Psi^\pm\rangle = (|\Psi^L\rangle \pm |\Psi^R\rangle)/\sqrt{2}$. If now the potential barrier is very high (negligible tunnel effect), enantiomorphic left- and right-handed species are stable and handedness as parity is a good quantum number for energy eigenstates.

Due to the parity violating weak interaction, the Hamiltonian matrix will remain diagonal only in the handedness-eigenstate basis and energy degeneracy lifting:

$$\begin{aligned} 2|E^{PV}| &= |\langle\Psi^L|H^{PV}|\Psi^L\rangle - \langle\Psi^R|H^{PV}|\Psi^R\rangle| \\ &= 2|\langle\Psi^-|H^{PV}|\Psi^+\rangle| \end{aligned}$$

appears between left and right enantiomers.

1.1.1 Physical origin of the lifting of degeneracy

The main term of the parity-violation Hamiltonian in atoms is [2] (for more details see also [10]):

$$H^{PV} \approx \frac{G_F}{2\sqrt{2}m_e c} \mathbf{s} \left[\mathbf{p} \delta^{(3)}(\mathbf{r}) \right]_+ Q_W \quad (1)$$

where G_F is the Fermi constant ($1.43 \times 10^{-62} \text{ J m}^3$), m_e the electron mass, $\mathbf{s} = \boldsymbol{\sigma}/2$ the dimensionless electron spin operator, \mathbf{p} the electron momentum operator. Q_W is the weak charge of the nucleus equal to $Z(1 - 4\sin^2\theta_W) - N$, Z and N are the proton and neutron numbers and where the Weinberg angle θ_W enters *via* $\sin^2\theta_W \approx 0.2236$.

From this elementary Hamiltonian the matrix element calculated between atomic orbitals $|ns_{1/2}\rangle$ and $|n'p_{1/2}\rangle$ increases like $Z^2 Q_W \approx Z^3$.

In the molecular case at the non-relativistic limit $\langle\varphi_0^R|H^{PV}|\varphi_0^R\rangle = \langle\varphi_0^L|H^{PV}|\varphi_0^L\rangle = 0$. Therefore, one has to consider a higher order term to obtain a non vanishing parity violating contribution. The largest second-order cross term implies the spin-orbit coupling [5,11]:

$$\begin{aligned} E_{\text{el}}^{\text{PV}} &= \langle\varphi_0|H^{\text{PV}}|\varphi_0\rangle \\ &= 2\text{Re} \left\{ \sum_{n \neq 0} \frac{\langle^1\varphi_0|H^{\text{SO}}|^3\varphi_n\rangle \langle^3\varphi_n|H^{\text{PV}}|^1\varphi_0\rangle}{^1E_0 - ^3E_n} \right\} \quad (2) \end{aligned}$$

where H^{PV} and H^{SO} couple a singlet state $|^1\varphi_0\rangle$ only to the triplet manifold $|^3\varphi_n\rangle$. An estimation of the spin-orbit contribution obtained from the multi-electron case shows a quadratic dependence with Z . $E_{\text{el}}^{\text{PV}}$ is the sum of different contributions which involve the pairs of nuclei of the molecule (the terms involving identical nuclei have a negligible contribution) [12]. Finally, the evaluation of $E_{\text{el}}^{\text{PV}}$ (Eq. (2)) leads to:

$$E_{\text{el}}^{\text{PV}} \approx 10^{-20} \eta Z_\alpha^2 Z_\beta^3 \text{ Hartree with } \alpha \neq \beta \quad (3)$$

where $10^{-4} < \eta < 10^{-2}$ is an asymmetry factor, which takes into account the chiral molecular environment around the nucleus of charge Z_β which is considered [13].

1.1.2 Quantum chemistry calculations

Since the 80's, many *ab initio* calculations have been performed on biological molecules [14]. Thus, the natural species of α -amino acids (as L-glycine, alanine, valine, serine) were found to be more stable with a lower electroweak energy ($E_{\text{el}}^{\text{PV}} \approx (-0.84 \text{ to } -2.29) \times 10^{-20}$ u.a.). These results gave credit to the speculations in biochemistry. Electroweak quantum-chemical studies (coupled Hartree-Fock method) confirmed the sign of the previous results but gave an amplitude of the effect larger by more than one order of magnitude [15–19]. However, recent calculated parity-violating energy shifts for 13 stable conformers of gaseous alanine indicate that the stabilization of a certain enantiomer is strongly dependent on its conformation (L-alanine is preferred for only 7 structures) [20]. Recent considerations suggested also that a possible answer of biomolecular homochirality could be obtained by considering rather kinetic effects at work during chemical synthesis of chiral molecules (related to the relative stability of certain possible prebiotic precursors) than the different thermodynamical stability of the mirror-image reaction products [21].

In all these calculations, only the perturbation of the electronic energy is taken into account. However, an argument of Letokhov [22] suggested that the relative difference of vibrational and rotational frequencies between left- and right-handed molecules is comparable to the electronic energy case:

$$\frac{E_{\text{el}}^{\text{PV}}}{E_{\text{el}}} \approx \frac{E_{\text{vib}}^{\text{PV}}}{E_{\text{vib}}} \approx \frac{E_{\text{rot}}^{\text{PV}}}{E_{\text{rot}}} \quad (4)$$

This qualitative argument is in favor of the vibrational spectroscopy which generally permits higher relative sensitivities. One must also mention other spectroscopic proposals [23–25] to observe a parity violation effect in molecules.

However, before our work, no calculation on vibrational shifts in any molecules was available. After the publication of our first results, three groups published independently vibrational frequency shifts corresponding to the C-F stretching mode of CHFCIBr (our experimental situation) but also of other asymmetric carbons [26–29].

Table 1. Calculated energy and frequency differences in CHFClBr according different authors.

Parity shift	[28]	[26, 29]	[30]
$\Delta_{\text{PV}}\nu_{\text{vib}}/\nu_{\text{vib}}$			
harmonic potential approx. \rightarrow	5×10^{-17}	6×10^{-17}	5.6×10^{-17}
anharmonic potential \rightarrow		-8×10^{-17}	-5.2×10^{-17}
$\nu_R - \nu_S$ (mHz)			
harmonic potential approx. \rightarrow	1.77	2	1.8
anharmonic potential \rightarrow		-2.6	-1.7
$\Delta_{\text{PV}}E/h$ (mHz)			
	74 [21]	58	69
$\Delta_{\text{PV}}\nu_{\text{rot}}/\nu_{\text{rot}}$			
		$1-3 \times 10^{-17}$	

More precise calculations have been recently performed for the C-F vibrational mode of a set of asymmetric carbons [30].

Explicit calculation of the second-order cross term due to the spin-orbit coupling (Eq. (2)) is necessary only within a non relativistic approach. In a fully relativistic treatment, as reported in [27], the parity violating energy shift is calculated as the matrix element:

$$E_{\text{el}}^{\text{PV}} = \langle \text{rel.} \varphi_0 | H^{\text{PV,rel.}} | \text{rel.} \varphi_0 \rangle \quad (5)$$

$E_{\text{el}}^{\text{PV}}$ (Eq. (2) or (5)), assumed to be diagonal (no coupling between different vibrational modes), is calculated as a function of the nuclear geometry and fitted to a polynomial expansion: $E_{\text{el}}^{\text{PV}}(Q_i) = \sum_{k=0}^n p_k(i) Q_i^k$; where Q_i denotes the set of normal coordinates.

$E_{\text{el}}^{\text{PV}}$ represents a small perturbation of the zero-order Hamiltonian H_0 . A first-order perturbation treatment leads to the energy shift $E_{\text{vib}}^{\text{PV}(1)} \approx \langle \phi_n | E_{\text{el}}^{\text{PV}}(Q_i) | \phi_n \rangle$, where $|\phi_n\rangle$ denotes the eigenfunction of H_0 and where the first correction to the vibrational frequency is proportional to the second derivative of the potential $E_{\text{el}}^{\text{PV}}(Q_i)$ versus molecular deformation. In [26, 29] the first contribution to the anharmonicity of the electronic potential is also taken into account. The main conclusions of the three evaluations of:

$$\Delta_{\text{PV}}h\nu_{\text{vib}} = [\text{R}E_{\text{vib}}^{\text{PV}}(\nu=1) - \text{R}E_{\text{vib}}^{\text{PV}}(\nu=0)] - [\text{S}E_{\text{vib}}^{\text{PV}}(\nu=1) - \text{S}E_{\text{vib}}^{\text{PV}}(\nu=0)] \quad (6)$$

for the C-F stretching are summarized in Table 1. For this particular case, the contribution due to the anharmonicity is more important because of an accidental quasi-cancellation of the first term.

1.2 Experimental background

In 1976 it was suggested that the observation of a frequency difference of two lasers stabilized onto the saturation resonances of the enantiomers of a chiral molecule would give a signature of a parity violation effect [31]. The CHFClBr molecule [31] was proposed as a good candidate because it is a heavy molecule with a strong absorption band in the tuning range of the CO₂ laser. However,

for the highest sensitivity, the method requires a physical separation of the enantiomers which was not achieved at that time in spite of efforts of chemists since the end of last century [32] and this blocked such an experiment with this molecule. A first attempt using this method was made in 1977 by Arimondo *et al.* [33]. They compared the rovibrational transitions in the separated isomers of camphor by measuring the inverted Lamb dips. The difference frequency was found to be zero within 300 kHz ($\Delta\nu/\nu = 10^{-8}$). The first efficient resolution of CHFClBr was finally achieved in 1989 [34] and confirmed by the group of Collet who established the link between the absolute configuration and the rotatory power of the molecule: $S-(+)$ and $R-(-)$ [35, 36]. They provided us a first series of samples (a few grams) with the following enantiomeric excesses (ee): $S-(+)$, $(22 \pm 2)\%$ and $R-(-)$, $(56.5 \pm 0.5)\%$ which permitted us to perform the first high sensitivity test of parity violation in molecules [9, 10].

Let us recall the principle of our experiment. A slightly different method than that proposed in 1976 has been applied [9, 10]: a single CO₂ laser feeds an electro-optic modulator (EOM) which generates sidebands (tunable between 0 and 500 MHz). One of these sidebands is frequency stabilized onto a saturation peak detected on the transmission signal of a 1.5 m long Fabry-Perot cavity (reference cavity). The frequency stabilization scheme is described in more detail elsewhere [37]. The stabilized laser carrier directly feeds two twin 3 m long Fabry-Perot cavities which are filled with the two enantiomers of CHFClBr. The spectra of the studied line can be recorded simultaneously since the carrier is tunable by tuning the frequency of the EOM. The principle of the test is to compare the frequencies of the line centers. It might be noted that the stability of the reference laser plays a negligible role in this experiment.

One hyperfine component of the ν_4 C-F stretching fundamental band of CHF³⁷Cl⁸¹Br (fully analyzed in [38]) was used for locking the laser side band. The test was performed on an unidentified hyperfine component with a peak-to-peak line width of 90 kHz and a signal-to-noise ratio of 300 over 30 ms. 580 measurements were performed over 10 days. A mean difference of 3.7 Hz with a standard deviation of 47 Hz and a final statistical uncertainty of 2 Hz is obtained. We had to include residual systematic effects in the final uncertainty although we could not detect them, we estimated them to 5 Hz. Finally, the difference

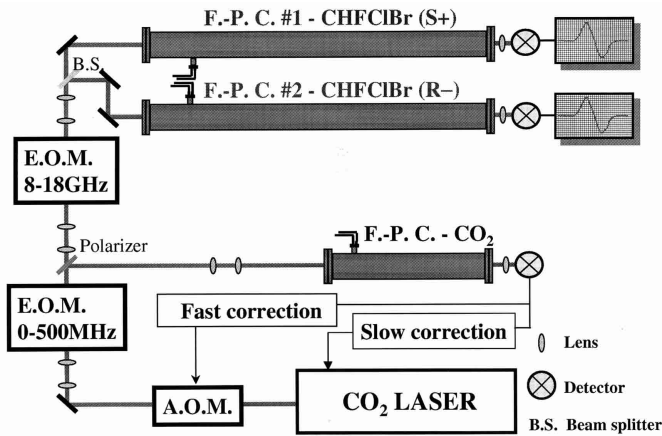


Fig. 2. Experimental set up used for the test.

between the eigenfrequencies of the two enantiomers are obtained when the enantiomeric excesses of the samples are taken into account (with statistical and systematic uncertainties): $\nu(R-) - \nu(S+) = 9.4 \pm 5.1 \pm 12.7$ Hz. So, no parity violation effect is observed at a relative sensitivity of $\Delta\nu/\nu = 3.9 \times 10^{-13}$, which is 5 orders of magnitude better than for the experiment on camphor [33].

2 New parity violation experiment

Then, we performed a new series of experiments in the spectrum of the enantiomers of CHFCIBr which improved the first one in several aspects. We obtained new samples with higher ee with which an even more sensitive test could be performed with a new experimental set up. Here we present our last efforts for observing a parity violating frequency shift. The experimental scheme was the following (Fig. 2): the CO₂ laser was optically isolated with a 40 MHz acousto-optic modulator (AOM) and is stabilized as described for the first series of experiments. However the reference molecular line chosen for this stabilization was the CO₂ laser line itself which gave directly a good knowledge of the absolute frequency of the studied CHFCIBr line. We implemented a second EOM, operating with a microwave between 8 and 18 GHz, on the path of the stabilized laser carrier just before two twin cavities. This provided a much broader tunability and permitted to access virtually to any rovibrational line of the various isotopic species of CHFCIBr. In addition, it was now possible to apply all modulations on the two EOM's and optimize the parameters of the reference line and the CHFCIBr line independently. The price is the small saturation power available due to the weak efficiency of the EOM (about 10^{-4} @ 20 W of microwave power) partly compensated by a higher laser power of 3 W (multiplied by 3 by changing the laser output coupler) and a higher finesse of 200 of the cavities (multiplied by 4). The characteristics of the cavities are now the following: a symmetric configuration with mirror radii of 50 m for the reference cavity and 100 m for the 3 m long twin cavities.

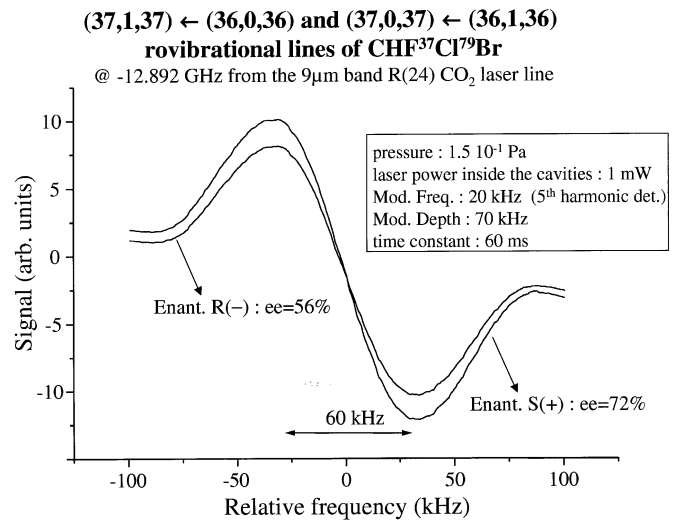


Fig. 3. Spectra of the test line. We checked that the intensity difference is mainly due to the difference of the sensitivity of the two detectors.

A new series of experiments whose principle is not different from the first one were then performed with samples of higher ee: $S - (+)$, 56% and $R - (-)$, 72%. We could perform an extensive analysis of the hyperfine structure of various isotopic species of CHFCIBr [39] and were able to find a much more favorable candidate. In fact, we found that the $(37, 1, 37) \leftarrow (36, 0, 36)$ and $(37, 0, 37) \leftarrow (36, 1, 36)$ rovibrational lines of CHF³⁷Cl⁷⁹Br which are highly degenerate and present an extremely compact hyperfine structure, show up in the Fabry-Perot cavities as a unique and highly symmetric line with a peak-to-peak width of 60 kHz¹. The optimized parameters were a pressure of 1.5×10^{-1} Pa with an equal pressure in both cavities controlled with a differential gauge at a 10^{-3} Pa level and a laser power of 1 mW inside the cavities. Despite the reduced power in the cavities (divided by 9), the signal-to-noise ratio about 1000 over 30 ms was significantly improved (Fig. 3). The CHFCIBr line was found at $-12\,891\,865.7$ (10) kHz from the R(24) CO₂ laser line which was used as the reference line which lead to a precise absolute calibration [40] of the CHFCIBr line: $32\,397\,293\,834.1(30)$ kHz.

3 Results

The difficulty of the experiment is to reduce as much as possible any systematic effect susceptible to simulate a parity violation effect. The experiment is a differential one which ensures an automatic compensation of a large fraction of these effects due to experimental imperfections such as modulation distortions, drift of the local oscillator, etc. In fact, the experiment is identical for the two kinds

¹ However, at the highest resolution for which the signal-to-noise ratio is strongly degraded, this line appears as a symmetric doublet with a splitting of 28 kHz.

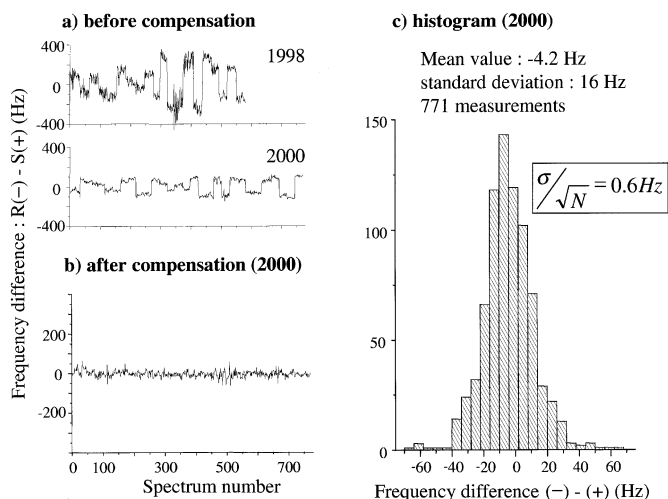


Fig. 4. (a) Crude frequency differences including measurements of 1998, (b) frequency differences after compensation of the daily systematic effects, (c) histogram of these compensated frequency differences.

of molecules until the 50/50 beamsplitter which separates the beam in two parts, directed towards the twin cavities. After that point, differences can occur but they can be partly compensated by an exchange of the role of the cavities. Most of the differences between the two cavities (in addition to the enantiomeric molecules themselves) which can induce an instrumental frequency difference, noticed f_{cavity} , are compensated by this exchange. However, it is important to avoid any chiral element in the experiment except the molecules themselves. In particular, the light polarization must be linear. This is ensured up to a few percent while no shift could be detected when a circular polarization was applied. An other source of uncompensated systematic effects could be a mirror image symmetry breaking due to different residual impurities in the two samples.

Practically, the cavities #1 and #2 are filled respectively with the enantiomers $S - (+)$ and $R - (-)$ in the morning and $R - (-)$ and $S - (+)$ in the afternoon. 771 measurements were performed over 15 days. The results of the measurements are presented in Figure 4a which represents the series of crude differences.

To illustrate the improvement of the present test, we also reported frequency measurements corresponding to our first search of parity violation performed in 1998. We retrieve the clear jump in the measurements at half-day that we attribute to systematic effects induced by uncontrolled differences in the two optical set up. These effects called f_{cavity} , are supposed to be constant over one day since we do not change any parameter. Thus, in the morning we measure $\Delta\nu + f_{\text{cavity}}$ and in the afternoon, $\Delta\nu - f_{\text{cavity}}$. The systematic error f_{cavity} can be calculated as half the difference of the mean values of the half-day measurements. Corrected values are obtained by subtracting this systematic part. We checked that these corrected values (Fig. 4b) present a white noise spectrum. The corresponding histogram (Fig. 4c) presents a clear Gaussian

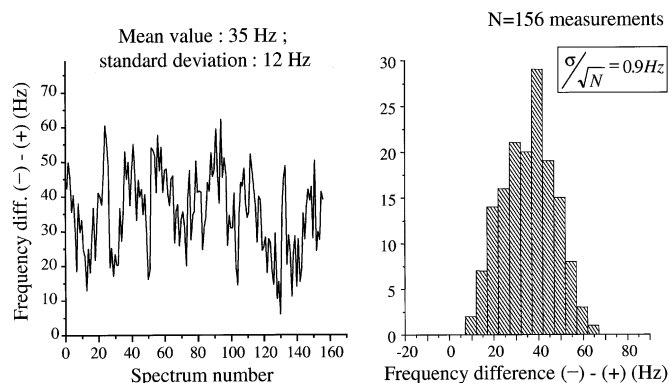


Fig. 5. Frequency difference obtained on the second test line with the samples $S - (+)(ee) = 56\%$ and $R - (-)(ee) = 56\%$.

shape. This is a strong indication that residual “cavity” systematic effects are a small fraction of the statistical error of an individual spectrum, *i.e.* 16 Hz.

Compared to the first series of experiments, the compensated systematic effects and the statistical noise are reduced by a factor at least 3. Finally, we obtained a histogram with a standard deviation of $\sigma = 16$ Hz (very close to the typical uncertainty given by the fit of an individual line) giving rise to a statistical uncertainty of $\sigma/\sqrt{N} = 0.6$ Hz while the mean frequency difference is found to be -4.2 Hz. The residual systematic effect of instrumental origin partially compensated by the inversion procedure described before have been estimated at 1.6 Hz. It is taken as one order of magnitude less than the uncertainty on one individual measurement. The resonance frequency difference associated to the two samples with statistical and systematic uncertainties is:

$$\Delta\nu = -4.2 \pm 0.6 \pm 1.6 \text{ Hz.} \quad (7)$$

This corresponds to a relative sensitivity for the frequency difference measurement of $\Delta\nu/\nu = 5 \times 10^{-14}$ (1/40 000 of the width of the signal *i.e.* 60 kHz).

The final frequency difference is high compared to the statistical and systematic uncertainties. Thus, we looked for an evidence of uncompensated systematic effects due to possible residual impurities in samples which can induce various collisional shifts. Since the impurities could be different, we can obtain an irreducible constant frequency difference, f_{sample} , whose signature would be a pressure dependence. Unfortunately because of the lack of product we could not use the new $R - (-)$ sample to check this hypothesis. For that reason, we performed the same test with the first sample of $R - (-)(ee) = 56.5\%$ and the second sample of $S - (+)(ee) = 56\%$ that we obtained. They were not prepared simultaneously. The frequency differences measured under the same conditions as previously (after compensation of the “cavity” systematic effects) are displayed in Figure 5. They reveal a clear and significant difference: $\nu(R-) - \nu(S+) = 35 \pm 0.9 \pm 1.3$ Hz. Same measurements have been performed during the first test, with a sample of racemic mixture and $R - (-)(ee) = 56.5\%$.

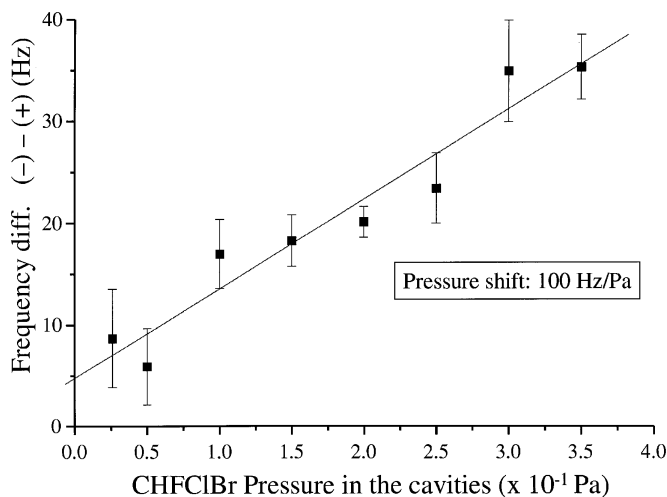


Fig. 6. Evidence for a differential pressure shift on the second test line obtained with the samples delivered in 1998.

We obtained $\nu(R-) - \nu(\text{Rac.}) = 41.2 \pm 4.3 \pm 5$ Hz. We suspected some residual impurities in the samples although they represent certainly less than 5% of CHFCIBr for $R - (-)$ and $S - (+)$ samples because the signals of the different samples were equal with this precision. However, between $R - (-)/S - (+)$ and the racemic sample, we observed a signal amplitude difference up to 30% attributed to large impurities in the racemic mixture. These could have been introduced during the preparation of the samples or their manipulation during the connection to the experiment.

In order to check this, we studied the pressure dependence of the shift. Because of the small fraction of new samples we used our old one and obtained a quite linear dependence of this shift with the pressure (Fig. 6) which cannot be a parity violation effect essentially independent on any external parameter. The extrapolated value at null pressure is +5 Hz with an uncertainty of 5 Hz. In fact, the shift of -4.2 Hz obtained at 0.15 Pa with the samples of 2000 is rather small which indicates that the fraction of impurities are probably smaller or much more identical in the new samples. The lack of molecules forbid the same extrapolation of the differential pressure shift to zero for the samples of 2000 which reduced the ultimate precision of our experiment by a factor 2 to 4.

It must be noticed that the samples from 1998 and 2000 gave similar signal amplitude within the experimental uncertainty of 5%. This gives a reasonable upper limit of the impurities in these samples. Considering 5 Hz as an upper limit of the residual uncertainty due to impurities (extrapolated value obtained with the samples of 1998 (Fig. 6) and shift obtained with the samples of 2000 (Fig. 4)), we can give a new upper limit for the frequency difference between the two enantiomers taken into account the enantiomeric excess of 56% and 72%:

$$|\nu_R - \nu_S| < 8 \text{ Hz} \Leftrightarrow |\Delta\nu/\nu| < 2.5 \times 10^{-13} \quad (8)$$

while the statistical uncertainty stays below 1 Hz.

4 Conclusion and perspectives

Our last set of experiments led to a significant improvement of the frequency difference sensitivity of 5×10^{-14} (compared to 1.6×10^{-13} in [9]). This allowed us to show evidence of a small but significant differential pressure shift of 100 Hz/Pa that we attributed to residual impurities of the samples. This last point gives probably an ultimate limit of the sensitivity for this experimental scheme. Let us suppose that we can improve by a factor 10 the purity of the samples in our cavities (fraction of impurity below 0.5%) which is probably the best that we can achieve with reasonable efforts. By extrapolation, we can expect an uncontrolled differential pressure shift of about 0.5 Hz ($\Delta\nu/\nu = 1.6 \times 10^{-14}$). This is already 10 times larger than the largest parity violation shift predicted on an asymmetric carbon by the most recent theoretical work [30]. Unless another molecule can lead to a much stronger effect, these limitations will prevent the observation of any parity violation effect with the present set up. It is thus necessary to reconsider the experimental project in order to avoid these collisional effects. For this reason, it seems that a molecular beam experiment would be much more suitable since the collisions come mainly from the background gas in the vacuum chamber which can be maintained at a very low pressure. Thus, we estimate that the most promising scheme is to develop a two-photon Ramsey fringes experiment with a double beam of chiral molecules for which the same optical set-up could be used alternatively for the two beams of enantiomers. This would be an evolution of a set up using a supersonic beam of SF₆ [41] with which we obtained already a very high resolution (200 Hz peak-to-peak) and a high signal-to-noise ratio leading to a statistical uncertainty of $0.5 \text{ Hz}/\sqrt{\text{Hz}}$ for the line center. Such a set up is obviously much more favorable for canceling any spurious systematic effects. If we can obtain the same performance with chiral molecules, the parity violation effect should be observable on molecules as CHFClI or CHFBrI for which the effects have been calculated as 23.7 mHz and 50.8 mHz, respectively [30]. This project is however still a challenge because it pre-requires the resolution of a significant amount of enantiomers of these molecules, which has never been achieved up to now, and then, a heavy spectroscopic work for identifying well-suited two-photon transitions in the infrared.

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