

→ SPIE

Feb 2007

Search for a frequency difference in the spectrum of the enantiomers of chiral molecules: how to reach a sensitivity better than 10^{-14} ?

Ch. Chardonnet*, M. Ziskind, T. Marrel, Ch. Daussey, Ch.J. Bordé, Ch. Grain, L.F. Constantin, C.T. Nguyen, A. Shelkovnikov**, R.J. Butcher***, A. Amy-Klein
Laboratoire de Physique des Lasers, UMR 7538 C.N.R.S. – Université Paris 13

ABSTRACT

A series of two searches of a frequency difference in the vibrational spectrum of the enantiomers of CHFCIBr by using Fabry-Perot cavities is presented. No difference is observed within the present sensitivity of 10^{-13} . This experiment is limited by pressure shifts induced by uncontrolled impurities of the samples. We propose to use a two-photon Ramsey fringes scheme with a molecular beam to push the relative sensitivity much below 10^{-14} in the range where the effect is expected.

Keywords: parity violation, infrared molecular spectroscopy, ultra-high resolution spectroscopy, frequency standard

1. INTRODUCTION

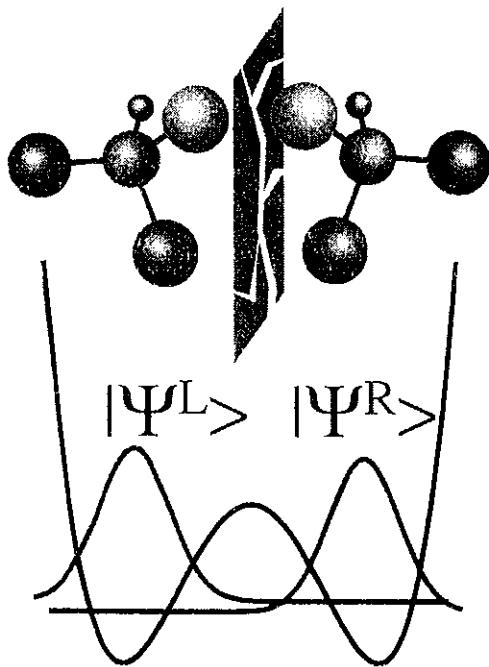


Figure 1: enantiomers of a chiral molecule are image each other in a mirror except if there is parity violation.

The weak interaction is the only fundamental interaction which does not respect left-right symmetry. This has been demonstrated for the first time by the famous experiment of β^- disintegration of the Co nucleus¹. 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 atoms². Although this interaction is of extreme short range, several precise experiments were achieved and confirmed the standard model³ to a high accuracy. 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 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 this symmetry breaking in the development of the prebiotic molecules and in the living systems is the subject of several controversial conjectures. Among these is the possibility that weak interaction is responsible for a slight energy difference in the spectrum of chiral molecules which could have favored the lowest energy chiral molecule. 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 other⁴.

This is one motivation of looking for a parity violation effect in molecules, which has never been observed so far. We present our efforts to observe a difference in the vibrational spectrum of the two enantiomers of CHFCIBr which is one of the simplest chiral molecules and which was suggested as a good candidate in 1976⁵.

* chardonnet@lpl.univ-paris13.fr; phone 33 1 4940 3382; fax 33 1 4940 3200; http://www.lpl.univ-paris13.fr; Laboratoire de Physique des Lasers UMR 7538 C.N.R.S.-Université Paris 13, Avenue J.B. Clément 93430 Villetaneuse, France

** permanent address: Lebedev Physical Institute – Troitsk - Russia

*** permanent address: Cavendish Laboratory – University of Cambridge – UK

2. THEORETICAL BASIS

2.1 left-right energy difference

Consider two left and right-handed states $|\Psi^{L,R}\rangle$ of a chiral molecule (Figure 1). If parity violation is neglected, these two states must have exactly the same energy E_0 . However, the molecule can change its configuration by tunnel effect. The Hamiltonian can be written as :

$$H = \begin{pmatrix} E_0 & \delta \\ \delta^* & E_0 \end{pmatrix} \quad (1)$$

The eigenstates are the states of well-defined parities :

$$|\Psi^\pm\rangle = \frac{1}{\sqrt{2}} (|\Psi^L\rangle \pm |\Psi^R\rangle) \quad (2)$$

With respective energies $E_0 \pm |\delta|$.

If now the tunnel effect is negligible, which is true for stable chiral molecules, the left-right character is a good quantum number. If there is parity violation, the Hamiltonian in the basis $\{|\Psi^\pm\rangle\}$ is written:

$$H = \begin{pmatrix} E_0 & \varepsilon \\ \varepsilon^* & E_0 \end{pmatrix} \quad (3)$$

The eigenstates of which are the left and right states $|\Psi^{L,R}\rangle$ of energies $E_0 \pm |\varepsilon|$. This lifting of degeneracy, provoked by the parity-violating term H^{PV} of the Hamiltonian is:

$$2|\Delta E^{PV}| = 2|\varepsilon| = 2|\langle\Psi^-|H^{PV}|\Psi^+\rangle| \quad (4)$$

2.2 Physical origin of the lifting of degeneracy

The expression of the parity-violation Hamiltonian in atoms was firstly derived by Bouchiat in 1974². The main term is:

$$H^{PV} \approx \frac{G_F}{2\sqrt{2}m_e c} \vec{s} \cdot [\vec{p} \otimes \delta^{(3)}(\vec{r})]_+ Q_W \quad (5)$$

G_F is the Fermi constant ($1.43 \cdot 10^{-62} \text{ J.m}^3$), m_e is the electron mass, $\vec{s} = \vec{\sigma}/2$ is the dimensionless electron spin operator, \vec{p} is the electron momentum operator. Q_W is the weak charge of the nucleus given by:

$$Q_W = Z(1 - 4 \sin^2 \theta_w) - N \quad (6)$$

where Z et 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 between atomic orbitals $|n s_{1/2}\rangle$ and $|n' p_{1/2}\rangle$ is:

$$\langle n s_{1/2} | H^{PV} | n' p_{1/2} \rangle \approx \left(\frac{i}{4\sqrt{2}\pi} \right) \frac{K_{rel.}}{(n^* n'^*)^{3/2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) m_e c^2 \alpha^2 Z^2 Q_W \quad (7)$$

Where n^* et n'^* are effective radial quantum numbers and $K_{rel.}$ is a relativistic correction factor which increases with Z. In the molecular case at the non-relativistic limit:

$$\langle 0^R | H^{PV} | 0^R \rangle = \langle 0^L | H^{PV} | 0^L \rangle = 0 \quad (8)$$

Because the electronic wave function can be chosen real and the operator \vec{p} is purely imaginary, which respects the time reversal invariance. A non-zero contribution is obtained if one considers the spin-orbit coupling which mixes the fundamental and excited states^{6,7}:

$$|0^\pm\rangle = |0^\pm\rangle + \sum_{n \neq 0} \frac{\langle n^\pm | H^{SO} | 0^\pm \rangle}{E_0 - E_n} |n^\pm\rangle \quad (9)$$

This leads to a non-zero second-order coupling term:

$$\varepsilon = \langle 0^- | H^{PV} | 0^+ \rangle = \sum_{n \neq 0} \frac{\langle 0^- | H^{PV} | n^+ \rangle \langle n^+ | H^{SO} | 0^+ \rangle}{E_0 - E_n} + \frac{\langle 0^- | H^{SO} | n^- \rangle \langle n^- | H^{PV} | 0^+ \rangle}{E_0 - E_n} \quad (10)$$

An estimation of the spin-orbit contribution can be obtained from the multi-electron case:

$$\Delta E_{jm}^{SO} = \langle n(ls) jm | H^{SO} | n(ls) jm \rangle = \zeta_{nl} [j(j+1) - l(l+1) - s(s+1)]/2 \quad (11)$$

where:

$$\zeta_{nl} = \alpha^2 \frac{Z_\alpha^2 H_r (Z_\alpha)}{n^3 l(l+1)(l+1/2)} Ry \quad h^* \quad (12)$$

Z_α is the effective charge of the nucleus and H_r is a relativistic correction. Ry represents the Rydberg constant. The order of magnitude of the energy ΔE^{PV} given by Eq. 10 is obtained by combining the Eqs. 7, 11 et 12:

$$\Delta E^{PV} \approx \eta \left(\frac{G_F m_e^2 c}{\hbar^3} \right) \alpha^4 Z^4 Q_w Ry \approx 10^{-20} \eta Z^5 \text{ Hartree} \quad (13)$$

where η is an asymmetry factor which takes into account the chiral molecular environment around the nucleus of charge Z which is considered. This factor, introduced for the first time by Zel'dovich⁸, varies from 10^{-2} to 10^{-4} . A more detailed study reveals that the energy ΔE^{PV} is the sum of different contributions which involve the pairs of nuclei of the molecule which lead to a $Z_\alpha^3 Z_\beta^2$ dependence. In addition, the terms such as $\alpha = \beta$ (identical nuclei) have a negligible contribution⁹.

2.3 Quantum chemistry calculations

Since the 80's, many ab initio calculations have been performed on biological molecules¹⁰. Thus, the natural species of α -amino acids (as L- glycine, alanine, valine, sérine) were found to be more stable with a lower electroweak energy ($\Delta E^{PV} \approx (-0.84 \text{ to } -2.29) \times 10^{-20}$ a.u.). These results gave credit to the speculations in biochemistry. More recent calculations (coupled Hartree-Fock method) confirmed the sign of the previous results but gave the amplitude of the effect larger by more than one order of magnitude¹¹⁻¹³. In these calculations, only the perturbation of the electronic energy is taken into account. However, an argument of Letokhov¹⁴ suggested that the relative difference of vibrational and rotational frequencies between left and right-handed molecules is comparable to the electronic energy case:

$$\frac{\Delta E_{el}^{PV}}{E_{el}^{PV}} \approx \frac{\Delta E_{vib}^{PV}}{E_{vib}^{PV}} \approx \frac{\Delta E_{rot}^{PV}}{E_{rot}^{PV}} \quad (14)$$

This qualitative argument is in favor the vibrational spectroscopy which generally permits higher relative sensitivities. One must also mention other spectroscopic attempts^{15,16} 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 theoretical groups published independently vibrational frequency shifts corresponding to the C-F stretching mode of CHFClBr (our experimental situation) but also of other asymmetric carbons. We summarize the main conclusions in the following table:

		R.G. Viglione et al. ¹⁷	M. Quack et al. ^{18,19}	J.K. Laerdahl et al. ²⁰
CHFClBr C-F Mode	$\frac{\Delta_{PV}^{V_{vib}}}{V_{vib}}$	$5 \cdot 10^{-17}$	$-8 \cdot 10^{-17}$	$-6 \cdot 10^{-17}$
	$V_R - V_S$	1,76 mHz	-2,6 mHz	-2,0 mHz (1,8 mHz)

not to be confused
with the amplification

	$\frac{\Delta_{(pv)}^S E}{h}$		58 mHz	70 mHz
	$\frac{\Delta_{(pv)}^R \nu_{rot}}{\nu_{rot}}$		$1-3 \cdot 10^{-17}$	
CHFBrI C-F Mode	$\nu_R - \nu_S$			-35,8 mHz
CHFBrI C-Br Mode	$\nu_R - \nu_S$	part		-180 mHz

3rd

The first column and the number in parenthesis in the third column are obtained with the harmonic potential approximation. The last column corresponds to a relativistic treatment. These converging results published after our experimental work indicate that a better choice would be the CHFBrI molecule.

3. PARITY VIOLATION TEST IN THE SPECTRUM OF CHFClBr

In 1976 was proposed, for the first time, 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 effect⁵. A first attempt using this method was made on camphor, but with a sensitivity of 10^{-8} which is far from that required²¹. The CHFClBr molecule was proposed as a good candidate because it is a heavy molecule with a strong absorption band in the range of the CO₂ laser. However, 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 century²² and this blocked any experiment with this molecule. The first efficient resolution was finally achieved in 1989²³ and confirmed by the group of A. Collet who established the link between the absolute configuration and the rotatory power of the molecule : S-(+) and R-(-)^{24,25}. It 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. Later we obtained new samples in 1998 in 2000 with the respective (ee) of 56% and 72% with which an even more sensitive test could be performed with the same experimental set up.

3.1 Principle of the experiment

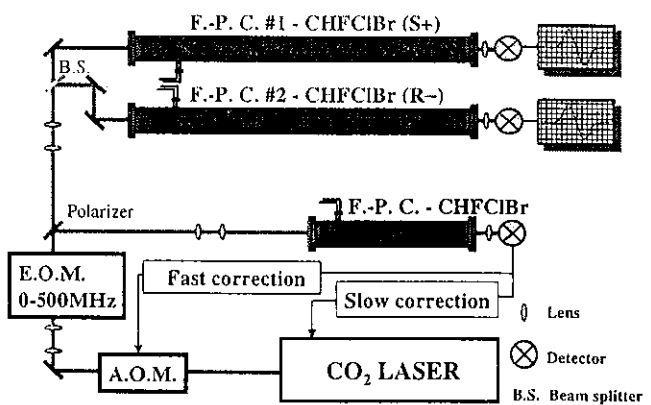


Figure 2 : experimental set up used for the first test

A slightly different method than that proposed in 1976 has been applied (Figure 2)^{26,27}: we used a CO₂ laser whose frequency is shifted by 40MHz by an acousto-optic modulator (AOM) for optical isolation purpose. The side band generated by an electro-optic modulator (EOM), tunable between 0 and 500 MHz, was stabilized onto a saturation peak detected on the transmission signal of a 1.5 m long Fabry-Perot cavity. The stabilized laser carrier directly fed two twin 3 m long Fabry-Perot cavities which were filled with the two enantiomers of CHFClBr. The spectra of the studied line could be recorded simultaneously since the carrier was tuned 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.
(limited)

3.2 First series of experiments

For the first test, the finesse of the cavities was only 50 (because the optics was optimized for 10.6 and not 9.4 μm). One hyperfine component of the $(39,8,31) \leftarrow (39,9,30)$ rovibrational transition of CHF³⁷Cl⁸¹Br located at -141.630MHz from the laser carrier in the vicinity of the R(14) line (9.4 μm band) of the CO₂ laser was used for locking the laser side band. In the reference cavity, the pressure was $2.7 \cdot 10^{-1}$ Pa and the laser power was 2 mW. The modulations were applied inside the laser cavity via PZT transducers for both the locking system and the experiment itself, the parameters being chosen to favor the detection of the test lines. For locking the Fabry-Perot cavities a first harmonic detection of a FM@41kHz was used

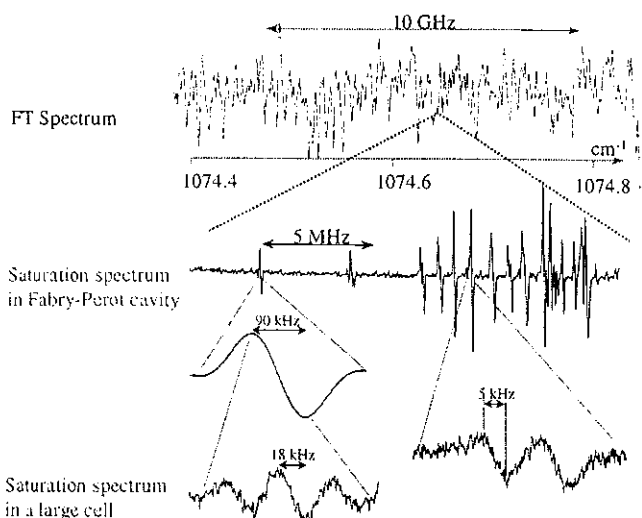


Figure 3 : CHFCIBr vibrational spectrum observed at various resolutions. The line used for the first test is the 90 kHz width line which presents an unresolved hyperfine structure.

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. 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. 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.

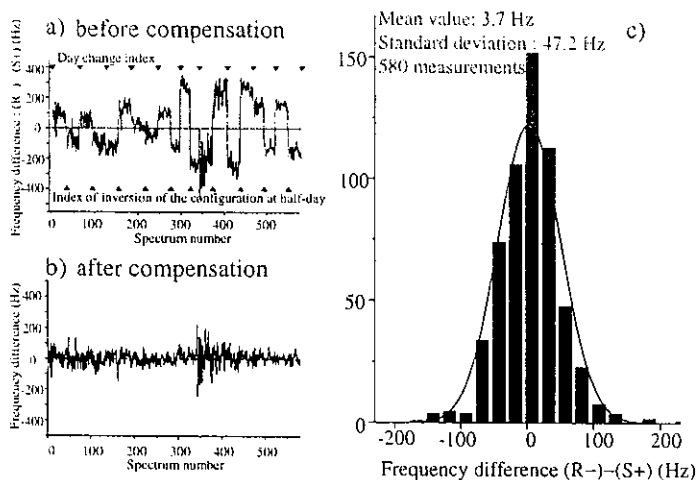


Figure 4 : a. crude frequency differences. b. frequency differences after compensation of the daily systematic effects. c. histogram of these compensated frequency differences

are a small fraction of the statistical error of an individual spectrum, i.e. 50Hz.

A mean difference of 3.7Hz with a standard deviation of 47Hz is obtained. σ is very close to the typical uncertainty given by the fit of an individual line. The final statistical uncertainty is $\frac{\sigma}{\sqrt{N-1}} \approx 2\text{Hz}$ where $N=580$ is the number of

measurements and 1 the number of parameters. We need to include residual systematic effects in the final uncertainty although we could not detect them. An estimate is 5 Hz since there are certainly much smaller than 50 Hz as already explained. Finally, we obtained a resonance frequency difference associated to the two samples with statistical and systematic uncertainties:

$$\Delta\nu = 3.7 \pm 2 \pm 5\text{Hz} \quad (15)$$

while a third harmonic detection of the FM@12kHz was preferred for the detection of the molecular signals. The test was performed on an unidentified hyperfine component very close to the structures of the $(40,7,34) \leftarrow (40,8,33)$ and $(49,10,39) \leftarrow (49,11,38)$ rovibrational lines. The optimized parameters were a pressure of 2.10^{-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 9mW inside the cavities. This line (Figure 3) recorded in the Fabry-Perot cavities with a peak-peak width of 90 kHz revealed an unresolved hyperfine structure in our large cell which can provide a typical resolution of 1 kHz.

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 systematic 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 of molecules until the 50/50 beamsplitter

580 measurements were performed over 10 days. The results of the measurements are presented on Figure 4 which represents the series of crude differences. There is clearly a jump in the measurements at half-day that we attribute to systematic effects induced by uncontrolled differences in the two optical set up. The systematic effects are supposed constant over one day since we do not change any parameter, any alignment,... Thus, in the morning we measure $\Delta\nu + f_{\text{sys}}$ and in the afternoon, $\Delta\nu - f_{\text{sys}}$ where f_{sys} represents the mean systematic error over the corresponding day which can be calculated as half the difference of the mean values of the half-day measurements. Corrected values are obtained by subtracting the systematic part. These values (Figure 4.b) present a white noise spectrum. The corresponding histogram (Figure 4.c) presents a clear Gaussian shape. This is a strong indication that residual systematic effects

The difference between the eigenfrequencies of the two enantiomers are obtained when the enantiomeric excesses of the samples are taken into account:

$$\nu(R-) - \nu(S+) = 9.4 \pm 5.1 \pm 12.7 \text{ Hz} \quad (16)$$

So, no parity violation effect is observed at a relative sensitivity of $\Delta\nu/\nu = 3.9 \cdot 10^{-13}$, which is 4 orders of magnitude lower than the test on camphor²¹. However, this is still far from the required sensitivity estimated by theoretical calculations presented in §2.3 which were published after our present work.

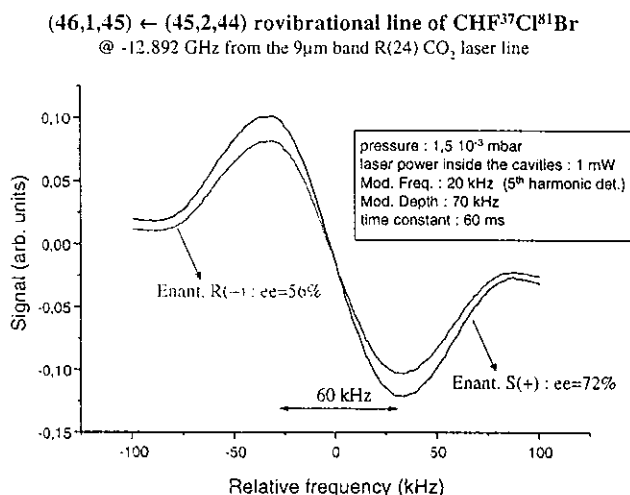


Figure 5: spectra of the second test line recorded with the two new samples. We checked that the intensity difference is mainly due to the difference of the sensitivity of the two photodetectors

line. The price is the weak efficiency of the EOM at 9μm (about 10⁻⁴@20W of microwave power) partly compensated by the higher laser power and the higher finesse of the cavities. We could perform an extensive analysis of the hyperfine structure of various isotopic species of CHFClBr²³ and were able to find a very favorable candidate for the new test. In fact, we found that the (46,1,45) ← (45,2,44) rovibrational line of CHF³⁷Cl⁸¹Br presents an extremely compact hyperfine structure which shows up in the Fabry-Perot cavities as a unique line with a peak-peak width of 60 kHz. Despite the reduced power in the cavities (1mW), the signal-to-noise ratio was significantly improved (Figure 5). We used the saturation signal of the R(24) CO₂ laser line as a reference line which gave a precise absolute calibration²⁹ of the CHFClBr test line found at -12891865.7(10) kHz from the CO₂ line.

Spine
Research

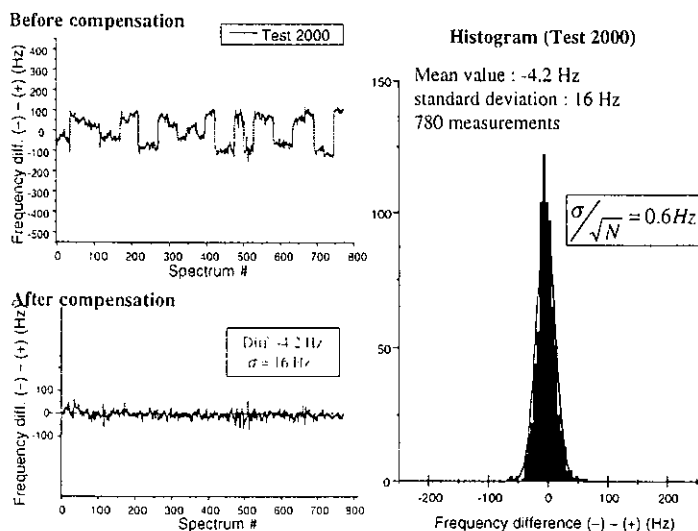


Figure 6: results obtained with the second test line (see Fig.4 for details)

3.3 Second series of experiments

The first attempt to observe a frequency difference in the spectrum of the enantiomers of CHFClBr could be certainly improved in several aspects. A new series of experiments whose principle is not different were then performed with samples of higher (ee) (cf. §3). The characteristics of the cavities are now the following: finesse of 200, symmetric configuration with mirror radii of 50 m for the reference cavity and 100 m for the 3 m long cavities. A change of the laser output coupler gave an available power (multiplied by 2) of 3 W. 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 allowed us to access virtually any rovibrational line of the various isotopic species of CHFClBr. In addition, it is now possible to apply all modulations on the two EOM's and adjust the parameters for the reference line and the test line independently and a 5th harmonic detection technique was applied for the test

Figure 6 summarizes the results obtained after 780 measurements recorded over 15 days. Compared to Figure 4, 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 16 Hz giving rise to a statistical uncertainty of 0.6Hz ($\Delta\nu/\nu = 2.10^{-14}$) while the mean frequency difference is found to be -4.2Hz. This difference is high compared to 0.6 Hz. We looked for evidence of systematic effects. For that purpose, 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 (after compensation of the "cavity" systematic effects) are displayed on Figure 7. They reveal a clear and significant difference. We suspected some residual impurities in the samples although they represent certainly less than 5% of CHFClBr

because the signals of the different samples are equal with this precision. These could have been introduced during the preparation of the samples or their manipulation for 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 (Figure 8) which cannot be a parity violation effect essentially independent of any external parameter.

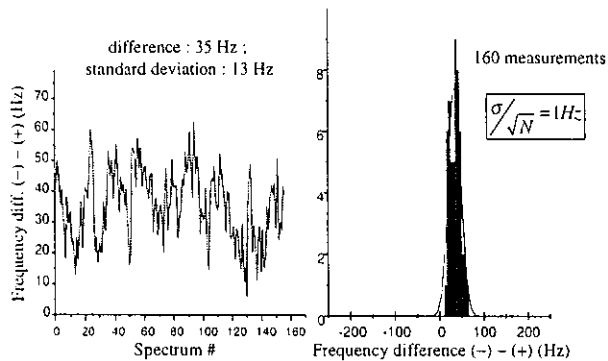


Figure 7: frequency difference obtained on the second test line with the sample S (-) (ee)= 56% of 1998 and (+) (ee)=56% of 2000.

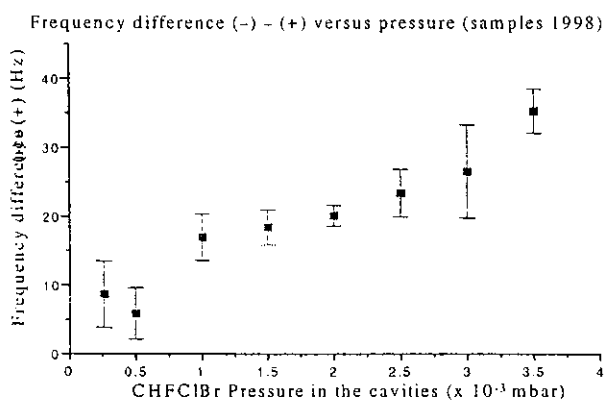


Figure 8: evidence for a differential pressure shift on the second test line obtained with the samples delivered in 1998.

3.4 Conclusion

The second set of experiments led to a significant improvement of the sensitivity in the range of a few parts in 10^{-14} . However, we were facing some systematic effects, of which a large fraction could be compensated by using the procedure of inversion of the role of the cavities. There remains, however, a differential pressure shift that we attributed to residual impurities of the samples. This last point gives, probably, an ultimate limit of 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 an upper limit ; by extrapolation, we can expect an uncontrolled differential pressure shift of about one Hz. This is already larger than the largest parity violation shift derived from the recent theoretical works²⁰. Unless another molecule can lead to a much stronger effect, the present limitations will prevent the observation of any parity violation effect.

It is thus necessary to re-consider the experimental project in order to avoid these pressure, that is collisional, effects. It would be also necessary to improve the resolution of the experiment and also to keep the signal-to-noise ratio. This would create the conditions of a strong reduction of most of the systematic effects which are proportional to the resolution. For this purpose, we propose to use a two-photon Ramsey fringes scheme with a supersonic beam of chiral molecules. In the last part of this paper, we present the first results that we obtained with a supersonic beam of SF_6 and indicate the new advantages and difficulties for the search of a frequency difference between enantiomers.

4. TWO-PHOTON RAMSEY FRINGES EXPERIMENT WITH A BEAM OF SF_6

For a search of frequency difference in the spectrum of chiral molecules we must certainly look for the highest resolution and the highest signal-to-noise ratio. These two features are usually incompatible and it is necessary to find a compromise. In infrared molecular spectroscopy, several schemes were extensively explored, mainly based on the saturated absorption method: in a large cell³⁰, in an external Fabry-Perot cavity³¹, different slow molecule detection methods^{32,33} and combinations with Ramsey fringes schemes³⁴. Doppler-free two-photon transitions were not considered mainly for practical reasons, i.e. the fundamental rovibrational bands of many simple molecules have been extensively studied while much less information is available for more excited vibrational bands. In this respect SF_6 is an exception since the rotational structure of the $2\nu_3$ band has been fully studied³⁵. It is then worth exploring the two-photon case because all velocity classes participate in the Doppler-free signal, by contrast with a saturation signal for which the longitudinal velocity classes around $v=0$ are more and more selected as the resolution increases so that the signal decreases very rapidly. This problem can be overcome by using separated fields, in a four zone geometry. The constraints on the parallelism and the equidistance of the pairs of zones limit practically the maximum distance between zones which, itself, is proportional to the resolution^{36,37}. For the two-photon case, the price to pay for the contribution of all velocity classes is a higher laser power as any intermediate state must be off resonance. This can increase the noise if an absorption detection is used. The problem is strongly reduced by using a high finesse Fabry-Perot cavity. It was noticeable that the slow molecule detection method

worked more efficiently in the two-photon case with a factor 23 of reduction of the line width (HWHM = 280 Hz) compared to the transit width because there is still no selection of the longitudinal velocity classes³⁸. However, the ultimate resolution was still limited by signal-to-noise ratio considerations.

The two-photon Ramsey fringes scheme is a very promising choice because we can hope to reach an extremely high resolution with a signal which decreases only slowly with the resolution.

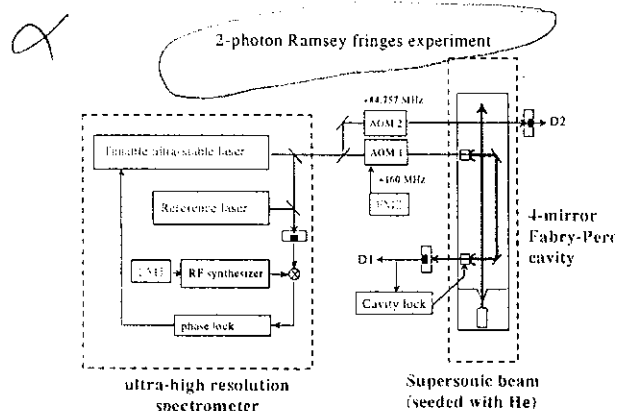


Figure 9: 2-photon Ramsey fringes experimental set up

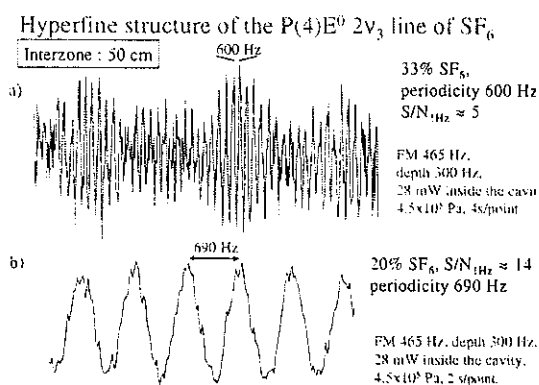


Figure 10: a. Ramsey fringes of various hyperfine components of the $P(4)E^0 2v_3$ line of SF_6 . b. Ramsey fringes of the strongest component (different concentration of SF_6).

4.1 Experiment

The principle of the experiment is simple (Figure 9)^{39,40}. We have studied the $P(4)E^0 2v_3$ two-photon transition with a supersonic beam of SF_6 . When the beam is seeded with helium, rotational cooling is enhanced and the population in the $J=4$ level increases significantly. It will interact with two standing waves generated within a four mirror Fabry-Perot cavity. This leads to fringes on the signal, with a periodicity equal to $u/2D$ where u is the mean velocity of the beam (400m/s for a pure SF_6 beam and 690m/s for a He-seeded beam with 20% SF_6) and D is the distance between zones. This distance is imposed by the position of the windows of the vacuum chamber and can be 10, 20, 30, 50, 100 and 180 cm. This geometry cancels automatically any relative phase between the two standing waves and guaranties that the central fringe is in coincidence with the molecular resonance. No strict parallelism of the zones is required and, thus, it is much easier to reach larger distances. The size of the signal is expected to decrease as the overlapping of the molecular and laser beams decreases in the two zones. The signal detection at the present stage is performed on the transmitted laser beam of the Fabry-Perot cavity. A modulation frequency of 465 Hz with a depth of 300 Hz is applied.

4.2 Results

So far, we performed this experiment with distances up to 50 cm. We were able to resolve the magnetic hyperfine structure of the transition (Figure 10.a with 33% SF_6 and a periodicity of 600 Hz). A typical signal-to-noise ratio of 14 and a periodicity of 690 Hz was obtained for the central component with 1s collection time using 20% SF_6 (Figure 10.b). This result is very promising if one considers that the low frequency detection of the absorption is very sensitive to the technical noise of the laser. In fact, the signal is very strong because it comes from a useful flux of 10^{10} - 10^{11} mol/s.

4.3 PERSPECTIVES

The molecular beam set up allows to implement an auxiliary detection laser beam in resonance with the one photon transition $v=2 \leftarrow v=1$ transition and to apply a high frequency modulation on this channel. By leaving the region of the technical noise, we can expect to reduce the noise by two orders of magnitude. Of course, this opens interesting possibilities for a new frequency standard in the $10\mu m$ region. If one reaches a $S/N_{1Hz}=500$ with the present resolution, we can expect a relative Allan variance of $4 \cdot 10^{-15}$ at 1s, an order of magnitude better than with a saturated resonance of OsO_4 which provides the best frequency standard in this spectral region. One can expect a much better long-term stability because of the much narrower width of the resonance. It must be noticed that this two photon Ramsey fringes experiment is in fact a molecular interferometer with an area which is exactly zero at resonance. By contrast with the so-called four zone Ramsey-Bordé interferometer, it is thus insensitive to external fields like gravity and earth rotation. The accuracy of such a standard will be certainly limited by the light shift and the second order Doppler effect. The light shift which is in fact proportional to the resolution has been measured to 10 Hz, the precision of which is limited by the available S/N. The second-order Doppler effect of 23 Hz can also be precisely deduced from a detailed analysis of the envelope of the fringes. However, this will be very likely the ultimate limitation of such a standard until effective slowing down methods of molecules is available.

or two nozzles:
3. Conclusion

This experiment might be adapted to a new search for frequency differences in the spectra of chiral molecules. Two main efforts are required in order to apply such an experiment to the parity violation project: the production in large quantity (~100g) of the resolved enantiomers of the test molecules and analysis of the rotational structure of the vibrational level $v=2$. These preliminary steps represent significant work but are feasible. After that, it will be necessary to adapt two reservoirs before the nozzle in order to produce alternatively a molecular beam with the left- and right-handed molecules. The set up will present numerous advantages compared to the present experiment: the resolution will be much higher with the possibility of resolving the complete hyperfine structure, the two beams will have almost identical interactions with the two standing waves and we expect a strong cancellation of a lot of systematic effects. Finally, the impurities in the samples are no more a difficulty since the collisions inside the beam or with the background gas are reduced by at least four orders of magnitude compared with the static Fabry-Perot cell. The sensitivity of such an experiment should be compatible with the observation of a parity violation effect in molecules.

ACKNOWLEDGEMENTS

This work has been sponsored by C.N.R.S., DGA and BNM. We are very grateful to A. Collet and J. Crassous for having provided us several samples of resolved enantiomers of CHFClBr.

REFERENCES

- ¹C.S. Wu, E. Ambler, R.W. Hayward *et al.*, "Experimental test of parity conservation in beta decay," *Physical Review* **105**, 1413-1415, 1957.
- ²M. A. Bouchiat, C. Bouchiat, "Weak neutral currents in atomic physics," *Phys. Lett.* **48B**, 111, 1974.
- ³C. S. Wood, S.C. Bennett, D. Cho *et al.*, "Measurement of parity nonconservation and an anapole moment in cesium," *Science* **275**, 1759-1763, 1997.
- ⁴D.K. Kondepudi, G.W. Nelson, "Weak neutral currents and the origin of biomolecular chirality," *Nature* **314**, 438-441, 1985.
- ⁵O.N. Kompanets, A.R. Kukudzhanov, V.S. Letokhov *et al.*, "Narrow resonances of saturated absorption of the asymmetrical molecule CHFClBr and the possibility of weak current detection in molecular physics," *Opt. Comm.* **19**, 414-416, 1976.
- ⁶E. Gajzago, G. Marx, "Energy difference of mirror molecules," *Atomki Kozlemenkev Suppl.* **16/2**, 177-184, 1974.
- ⁷D.W. Rein, "Some remarks on parity violating effects of intramolecular interactions," *J. Mol. Evol.* **4**, 15-22, 1974.
- ⁸B.Y. Zel'dovich, D.B. Saakyan, and I.I. Sobel'man, "Energy differences between right-hand and left-hand molecules, due to parity nonconservation in weak interactions of electrons with nuclei," *JETP Lett.* **25**, 94-97, 1977.
- ⁹R.A. Hegstrom, D.W. Rein, and P.G.H. Sandars, "Calculation of the parity nonconserving energy difference between mirror-image molecules," *J. Chem. Phys.* **73** (5), 2329-2341, 1980.
- ¹⁰S. F. Mason and G. E. Tranter, "The parity-violating energy difference between enantiomeric molecules," *Molecular Physics* **53** (5), 1091-1111, 1984.
- ¹¹P. Lazzeretti and R. Zanasi, *Chemical Physics Letters* **279**, 349, 1997.
- ¹²A. Bakasov, T.-K. Ha, and M. Quack, *Journal of Chemical Physics* **109**, 7263, 1998.
- ¹³R. Zanasi, P. Lazzeretti, A. Ligabue *et al.*, *Physical Review E* **59**, 3382, 1999.
- ¹⁴V.S. Letokhov, "On difference of energy levels of left and right molecules due to weak interactions," *Phys. Lett.* **53A**, 275, 1975.
- ¹⁵M. Quack, "On the measurement of the parity violating energy difference between enantiomers," *Phys. Lett.* **132**, 147, 1986.
- ¹⁶A.L. Barra and J.B. Robert, "Parity non-conservation and NMR parameters," *Mol. Phys.* **88**, 875, 1996.
- ¹⁷R.G. Vigiore, R. Zanasi, P. Lazzeretti *et al.*, "Theoretical determination of parity-violating vibrational frequency differences between the enantiomers of the CHFClBr molecule," *Physical Review A* **62** (5), 052516, 2000.
- ¹⁸M. Quack and J. Stohner, "On the influence of parity weak nuclear potentials on vibrational and rotational frequencies in chiral molecules," *Physical Review Letters* **84**, 3807-3811, 2000.

- ¹⁹M. Quack and J. Stohner, "How do parity violating weak nuclear interactions influence rovibrational frequencies in chiral molecules?," *Zeitschrift für Physikalische Chemie* **214** (5), 675-703, 2000.
- ²⁰J.K. Laerdahl, P. Schwerdtfeger, and H.M. Quiney, "Theoretical analysis of parity-violating energy differences between the enantiomers of chiral molecules," *Phys. Rev. Lett.* **84**, 3811, 2000.
- ²¹E. Arimondo, P. Glorieux, and T. Oka, "Observation of inverted infrared lamb dips in separated optical isomers," *Opt. Comm.* **23**, 369-372, 1977.
- ²²F. Swarts, *Bulletin de l'Académie Royale de Belgique* **26**, 102, 1893.
- ²³T.R. Doyle and O. Vogl, "Bromochlorofluoromethane and deuteriobromochlorofluoromethane of high optical purity," *Journal of American Chemical Society* **111** (22), 8510-8511, 1989.
- ²⁴J. Costante, L. Hecht, P.L. Polavarapu *et al.*, "Absolute configuration of bromochlorofluoromethane from experimental and ab initio theoretical vibrational Raman optical activity," *Angewandte Chemie* **36**, 885, 1997.
- ²⁵J. Costante-Crassous, T.J. Marrone, J.M. Briggs *et al.*, "Absolute configuration of bromochlorofluoromethane from molecular dynamics simulation of its enantioselective complexation by cryptophane-C," *Journal of American Chemical Society* **119**, 3818, 1997.
- ²⁶Ch. Chardonnet, Ch. Daussy, T. Marrel *et al.*, "Parity violation test in chiral molecules by laser spectroscopy," in *Parity violation in atomic physics and electron scattering*, edited by B. Frois and M.A. Bouchiat (World Scientific, New-York, 1999), pp. 325-355.
- ²⁷Ch. Daussy, T. Marrel, A. Amy-Klein *et al.*, "Limit on the parity nonconserving energy difference between the enantiomers of a chiral molecule by laser spectroscopy," *Physical Review Letters* **83**, 1554-1557, 1999.
- ²⁸T. Marrel, M. Ziskind, Ch. Daussy *et al.*, "High precision rovibrational and hyperfine analysis of the $\nu_4=1$ level of bromochlorofluoromethane," *Journal of Molecular Structure* **to be published**, 2001.
- ²⁹A.G. Maki, C.-C. Chou, K. Evenson *et al.*, "Improved molecular constants and frequencies for the CO₂ laser from new high-J regular and hot-band frequency measurements," *J. Mol. Spectrosc.* **167** (1), 211-224, 1994.
- ³⁰J.L. Hall, Ch.J. Bordé, and K. Uehara, "Direct optical resolution of the recoil effect using saturated absorption spectroscopy," *Physical Review Letters* **37** (20), 1339-1342, 1976.
- ³¹A. Clairon, B. Dahmani, A. Filimon *et al.*, *IEEE Trans. Instrum. Meas.* **IM-34**, 265, 1985.
- ³²S.N. Bagayev, A.E. Baklanov, V.P. Chebotayev *et al.*, "Superhigh resolution spectroscopy in methane with cold molecules," *Rev. Roum. Phys.* **33**, 361-367, 1988.
- ³³Ch. Chardonnet, F. Guernet, G. Charton *et al.*, "Ultrahigh-resolution saturation spectroscopy using slow molecules in an external cell," *Applied Physics B* **B59**, 333-343, 1994.
- ³⁴Ch.J. Bordé, Ch. Salomon, S. Avrillier *et al.*, "Optical Ramsey fringes with traveling waves," *Phys. Rev. A* **30**, 1836-1848, 1984.
- ³⁵M. Khelkhal, E. Rusinek, J. Legrand *et al.*, "Sub-Doppler study of the $\nu_3=2$ state of SF₆ by infrared-infrared double resonance with a sideband spectrometer," *Journal of Chemical Physics* **107** (15), 5694-5701, 1997.
- ³⁶Ch.J. Bordé, "Forme de raie en spectroscopie à deux quanta sans élargissement Doppler," *C. R. Acad. Sc. Paris* **282B**, 341-344, 1976.
- ³⁷Ye.V. Baklanov, V.P. Chebotayev, and B.Ya. Dubetsky, "The Resonance of Two-Photon Absorption in Separated Optical Fields," *Applied Physics* **11** (2), 201-202, 1976.
- ³⁸P.E. Durand, G. Noguez, V. Bernard *et al.*, "Slow-molecule detection in Doppler-free two-photon spectroscopy," *Europhysics Letters* **37**, 103-108, 1997.
- ³⁹L.F. Constantin, R.J. Butcher, P.E. Durand *et al.*, "2.3 kHz two-photon Ramsey fringes at 30 THz," *Physical Review A* **60** (2), 753-756, 1999.
- ⁴⁰A. Amy-Klein, L.F. Constantin, R.J. Butcher *et al.*, "High-resolution spectroscopy with a molecular beam at 10.6 μm ," *Physical Review A* **63** (01), 013404-1-8, 2000.