PARITY VIOLATION TEST IN CHIRAL MOLECULES BY LASER SPECTROSCOPY

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A laser nonlinear spectroscopy experiment has been designed and implemented to test the conjecture that enantiomers of chiral molecules may have different spectra because of the parity violation associated with neutral currents in the weak interaction between electrons and nuclei. We review the theoretical reasons that lead to this prediction and we outline the method currently used to calculate energy and frequency differences between mirror image molecules. Preliminary 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 identical within 13 Hz ($\Delta\nu/\nu$ <4. 10^{-13}).

1 Introduction and historical background

We address ourselves to the general problem of the role that parity-violation in weak interactions [1,2] and especially those associated with neutral currents [3,4,5], has in molecular physics. Besides consequences for all molecules [6−9]similar to those already known in atomic physics [10−19], a very interesting new feature comes from the fact that the molecular structure may be chiral and hence not correspond to a parity eigenstate. A difference in energy may then arise between mirror configurations of the molecule [20−29], depending on their handedness.

The specific question that we wish to raise in this paper, both from a theoretical and from an experimental point of view, is the following: **do enantiomers of chiral molecules have identical spectra in the absence of any external field[a]?** As an example, that we will consider in more detail later, two methane molecules substituted with four different atoms (Figure 1) should have exactly the same absorption frequencies if mirror symmetry was respected.

If parity is violated, this might not be true anymore and modern ultra-high resolution spectroscopy is able to test the difference with a very high accuracy

[a]The same question in presence of a large magnetic field, for nuclear magnetic resonance spectra, has been studied in detail by Gorshkov [30] and by Barra and coll. [31−34] and we will not consider this case here.

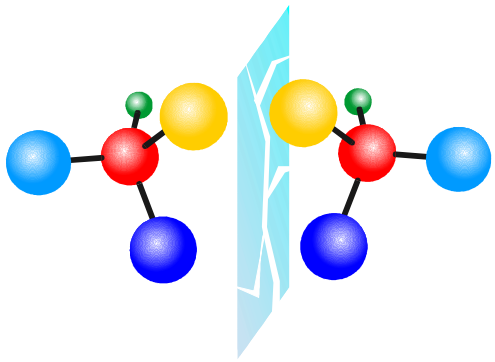

Figure 1: Because of parity violation in weak interactions enantiomorphic species may not be faithful mirror images and may have different spectra.

as we shall see [35,36].

The fact that parity violation could manifest itself in chiral molecules as an energy shift of opposite sign for the two enantiomers was first suggested by D.W. Rein [20] in September 1973, a few years only after the introduction of neutral currents in weak interactions [3,4,5]. It was later conjectured by V.S. Letokhov [24] that this difference in energies could manifest itself as a difference in vibrational or rotational frequencies. Many theoretical studies have been pursued to obtain quantitative estimates of the effect in various molecules and we shall outline one of these approaches, but none of them is yet able to provide even a crude estimate of the expected frequency shift. In this context, it was of great interest to perform an experiment. Another major issue is, of course, the possible role of the weak interaction in the emergence of the homochirality of L-$\alpha-$aminoacids and D-sugars associated with living organisms on earth [37−47].

2 Theoretical background

2.1 Parity and chirality

What is so special in chiral molecules that cannot be found in atoms and other molecules? **Chiral molecules may exist in states that differ only by their handedness or by their parity, all other quantum numbers being the same.** In other polyatomic molecules, we have shown, experimentally and theoretically [48,49,35], that, because of the Pauli principle, states which differ by their parity also differ by some other property of their wave functions, as it is the case also for atoms.

For chiral molecules, if $|\Psi^R\rangle$ is a possible state with a right-handed configuration, then, there exists also a state $|\Psi^L\rangle$ which is left-handed but otherwise identical. As we shall see, from this "handedness" basis one can construct two other states $|\Psi^{\pm}>$ which differ only by their parity. The potential energy curve for the chiral molecules is symbolically represented in Figure 2 as a function of the internuclear coordinate along which the molecule may invert itself. If the tunneling barrier is not too high, mirror symmetry is dynamically

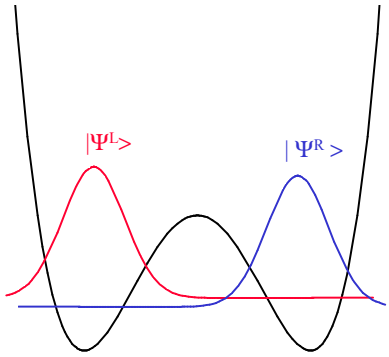

Figure 2: If the familiar double well potential curve exhibits a barrier of sufficient height, tunneling inversion between right and left-handed species may not occur and handedness is a good quantum number over long time scales. If parity is violated this figure loses its symmetry about the vertical axis.

restored by the inversion mechanism. Parity commutes with the Hamiltonian and energy eigenstates are parity-eigenstates. In the handedness-eigenstates basis the Hamiltonian matrix will have off-diagonal elements representing the tunneling coupling terms between the right and left-handed species:

$$H_H = \begin{pmatrix} E_0 & \delta \\ \delta^* & E_0 \end{pmatrix} \tag{1}$$

Going to the parity-eigenstates basis[b]:

$$|\Psi^{\pm}>= \frac{1}{\sqrt{2}}(|\Psi^R> \pm e^{i\varphi}|\Psi^L>) \tag{2}$$

[b]The phase φ, which appears in this combination, is the phase of the coupling matrix element δ (modulo π, because there is an ambiguity in the correspondence between parity-eigenstates and eigenvalues which can be resolved only by a more detailed knowledge of the Hamiltonian). Such a phase may manifest itself in the phase difference in a molecular interferometry experiment [50] in which, for example, Raman two-photon interactions convert enantiomers in their opposite form along each arm of the interferometer.

this coupling will remove the degeneracy of the energy eigenvalues of states of opposite parity:

$$H_P = \begin{pmatrix} E_0 + |\delta| & 0 \\ 0 & E_0 - |\delta| \end{pmatrix} \tag{3}$$

The handedness-eigenstates, which are superpositions of two parity eigenstates with different energies, are clearly time-dependent and chiral molecules tunnel back and forth between the right and left limiting forms.

On the other hand, if the potential barrier is very high, the molecule does not invert itself, the enantiomorphic left and right-handed species are stable and handedness is a good quantum number for energy eigenstates. If parity is violated, the Hamiltonian matrix which is not diagonal in the parity-eigenstates basis will remain diagonal in the handedness-eigenstates basis but the corresponding degeneracy will be removed:

$$H_P = \begin{pmatrix} E_0 & \varepsilon \\ \varepsilon^* & E_0 \end{pmatrix} \tag{4}$$

in the basis $|\Psi^{\mp}>$ becomes:

$$H_H = \begin{pmatrix} E_0 + |\varepsilon| & 0 \\ 0 & E_0 - |\varepsilon| \end{pmatrix} \tag{5}$$

with eigenvectors:

$$|\Psi^{R,L}>= \frac{1}{\sqrt{2}}(|\Psi^{+}> \pm e^{i\chi}|\Psi^{-}>) \tag{6}$$

An equivalent argument was followed by Rein [20]: let U_P be the mirror reflexion (parity) operator which transforms left-handed into right-handed states:

$$U_P|\Psi^{R,L}>= |\Psi^{L,R}> \tag{7}$$

then the corresponding energies are related by:

$$\left\langle \Psi^R \left| H^{PV} \right| \Psi^R \right\rangle = \left\langle \Psi^L \left| U_P^{-1} H^{PV} U_P \right| \Psi^L \right\rangle = - \left\langle \Psi^L \left| H^{PV} \right| \Psi^L \right\rangle \tag{8}$$

where

$$H^{PV} = -U_P^{-1} H^{PV} U_P$$

is the parity-violating part of the Hamiltonian and their difference is:

$$\begin{aligned} 2\left|\Delta E^{PV}\right| &= \left|\left\langle \Psi^L \left| H^{PV} \right| \Psi^L \right\rangle - \left\langle \Psi^R \left| H^{PV} \right| \Psi^R \right\rangle\right| \\ &= 2|\left\langle \Psi^- \left| H^{PV} \right| \Psi^+ \right\rangle| = 2\left|\varepsilon\right| \end{aligned} \tag{9}$$

We shall now briefly outline the calculation of ΔE^{PV} following the early approach of Rein, Hegstrom and Sandars [27,51].

2.2 The molecular Hamiltonian

2.2.1 The parity-violating Hamiltonian

The parity-violating part of the electron-nucleus interaction Hamiltonian may be written as [10,19,31]:

$$H^{PV} = H_1^{PV} + H_2^{PV} + H_3^{PV} \tag{10}$$

where:

$$H_1^{PV} = \frac{G_F}{2\sqrt{2}m_e c}\overrightarrow{s}.\left[\overrightarrow{p},\delta^{(3)}(\overrightarrow{r})\right]_+ \mathbf{Q}_W \tag{11}$$

is the dominant term. In this equation, G_F is the Fermi constant (1.43×10^{-62} J.m^3), m_e the electron rest mass, c the speed of light, $\overrightarrow{s} = \overrightarrow{\sigma}/2$ the dimensionless electron spin operator, $\left[\overrightarrow{p},\delta^{(3)}(\overrightarrow{r})\right]_+$ is the anticommutator of the electron momentum operator $\overrightarrow{p}$ and of the 3D Dirac distribution. Finally the nucleus has a weak charge given by:

$$\mathbf{Q}_W = \mathbf{Z}\left(1 - 4\sin^2\theta_W\right) - \mathbf{N}$$

where $\mathbf{Z}$ and $\mathbf{N}$ are respectively the proton and neutron numbers and where the Weinberg angle θ_W is given by $\sin^2\theta_W \simeq 0.2236$.

The next terms in the Hamiltonian:

$$\begin{aligned} H_2^{PV} &= -\lambda_N \frac{G_F}{2\sqrt{2}m_e c}\overrightarrow{I_N}.\left[\overrightarrow{p},\delta^{(3)}(\overrightarrow{r})\right]_+ \left(1 - 4\sin^2\theta_W\right) \\ H_3^{PV} &= i\lambda_N \frac{G_F}{\sqrt{2}m_e c}\left(\overrightarrow{s}\times\overrightarrow{I}_N\right).\left[\overrightarrow{p},\delta^{(3)}(\overrightarrow{r})\right]\left(1 - 4\sin^2\theta_W\right) \end{aligned} \tag{12}$$

with $\lambda_N \sim 1$ [12], depend on the nuclear spin operator $\overrightarrow{I}_N$, and they are usually neglected in atomic and molecular physics[c]. So, in the following, we shall consider only the first term and write the total parity-violating Hamiltonian as a sum of one-electron operators $\overrightarrow{s_i} = \overrightarrow{\sigma_i}/2$ and $\overrightarrow{p_i}$, where each nucleus α has a weak charge $\mathbf{Q}_W^\alpha$:

[c] One should also consider the anapole term introduced by Zel'dovich [52,53].

$$H^{PV} = \frac{G_F}{4\sqrt{2}m_e c}\sum_{i,\alpha}\overrightarrow{\sigma_i}.\left[\overrightarrow{p_i},\delta^{(3)}(\overrightarrow{r_{i\alpha}})\right]_+ \mathbf{Q}_W^\alpha$$
$$= \frac{1}{4\sqrt{2}}\left(\frac{G_F m_e^2 c}{\hbar^3}\alpha\right)\alpha(m_e c^2\alpha^2)$$
$$\left\{a_0^4\hbar^{-1}\sum_{i,\alpha}\overrightarrow{\sigma_i}.\left[\overrightarrow{p_i},\delta^{(3)}(\overrightarrow{r_{i\alpha}})\right]_+ \mathbf{Q}_W^\alpha\right\} \tag{13}$$

where:

$$\left(\frac{G_F m_e^2 c}{\hbar^3}\alpha\right) = \frac{G_F}{a_0^3(m_e c^2\alpha^2)} \simeq 2.2\ 10^{-14} \tag{14}$$

is usually taken as the dimensionless coupling constant and where we have introduced the atomic units of energy and distance:

$$m_e c^2\alpha^2 = 2Ry = 1 \text{ Hartree and } a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2} = \frac{1}{\alpha}\frac{\hbar}{m_e c} \tag{15}$$

We will need the matrix element of the Hamiltonian 13, which is easily obtained from:

$$\left\langle\varphi\left|\left[\overrightarrow{p},\delta^{(3)}(\overrightarrow{r})\right]_+\right|\varphi'\right\rangle = i\hbar\left[\varphi'(\overrightarrow{r})\overrightarrow{\nabla\varphi}(\overrightarrow{r}) - \varphi(\overrightarrow{r})\overrightarrow{\nabla\varphi'}(\overrightarrow{r})\right]_{(\overrightarrow{r}=0)} \tag{16}$$

In atoms, owing to its contact character, the parity-violating Hamiltonian may thus connect only s and p orbitals:

$$\left\langle n'p_z\left|\left[p_z,\delta^{(3)}(\overrightarrow{r})\right]_+\right|ns\right\rangle = \frac{i\hbar\sqrt{3}}{4\pi}R_{n0}(0)\left[\frac{d}{dr}R_{n'1}(r)\right]_{r=0} \tag{17}$$

and

$$\left\langle ns_{1/2}\left|H^{PV}\right|n'p_{1/2}\right\rangle = \frac{3i}{16\pi\sqrt{2}}\left(\frac{G_F m_e^2 c}{\hbar^3}\alpha^2\right)m_e c^2\alpha^2\mathbf{Q}_W$$
$$a_0^4 R_{n0}(0)\left[\frac{d}{dr}R_{n'1}(r)\right]_{r=0} \tag{18}$$

in the coupled $|\ (sl)j\rangle$ basis, where $R_{n0}(r)$ and $R_{n'1}(r)$ are respectively the radial parts of the ns and of the $n'p$ wave functions:

$$\varphi_{ns} = \frac{1}{\sqrt{4\pi}}R_{n0}(r) \qquad ; \qquad \varphi_{n'p} = Y_{1m}(\theta,\varphi)R_{n'1}(r).$$

These functions can be taken from the work of M.-A. Bouchiat and C. Bouchiat [10] and using their formulas, one gets:

$$\left\langle n'p_z \left| \left[p_z, \delta^{(3)}(\overrightarrow{r}) \right]_+ \right| ns \right\rangle \simeq (-1)^{n_*+n'_*-1} \left(\frac{i\hbar}{\pi\sqrt{3}a_0^4} \right) \frac{K_{rel.}}{(n_* n'_*)^{3/2}} \mathbf{Z}^2 \tag{19}$$

and

$$\left\langle ns_{1/2} \left| H^{PV} \right| n'p_{1/2} \right\rangle \simeq \left(\frac{i}{4\sqrt{2}\pi} \right) \frac{K_{rel.}}{(n_* n'_*)^{3/2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) m_e c^2 \alpha^2 \mathbf{Z}_\alpha^2 \mathbf{Q}_W \tag{20}$$

in the coupled basis, where n_*, n'_*, are effective radial quantum numbers and where $K_{rel.}$ is a relativistic correction factor increasing with $\mathbf{Z}$.

For molecules, in the nonrelativistic limit :

$$\left\langle 0^R \left| H^{PV} \right| 0^R \right\rangle = \left\langle 0^L \left| H^{PV} \right| 0^L \right\rangle = 0 \tag{21}$$

because the electronic wavefunction $\psi_0^{R,L} = \langle \overrightarrow{r} \mid 0^{R,L} \rangle$ may be chosen purely real, while $\overrightarrow{p_i}$ is purely imaginary as expected from time reversal invariance (one should remember that the Hamiltonian H^{PV} has time reversal symmetry). As pointed out by Gajzago and Marx [23] it is therefore necessary to invoke the spin-orbit coupling to mix the ground state $\mid 0^{\pm} \rangle$ with excited states $\mid n^{\pm} \rangle$:

$$\mid 0'^{\pm} \rangle = \mid 0^{\pm} \rangle + \sum_{n \neq 0} \frac{\left\langle n^{\pm} \left| H^{SO} \right| 0^{\pm} \right\rangle}{E_0 - E_n} \mid n^{\pm} \rangle \tag{22}$$

and to obtain a non-zero contribution at the second perturbation order:

$$\begin{aligned} \varepsilon = \left\langle 0'^{-} \left| H^{PV} \right| 0'^{+} \right\rangle = \sum_{n \neq 0} & \frac{\left\langle 0^{-} \left| H^{PV} \right| n^{+} \right\rangle \left\langle n^{+} \left| H^{SO} \right| 0^{+} \right\rangle}{E_0 - E_n} \\ + & \frac{\left\langle 0^{-} \left| H^{SO} \right| n^{-} \right\rangle \left\langle n^{-} \left| H^{PV} \right| 0^{+} \right\rangle}{E_0 - E_n} \end{aligned} \tag{23}$$

where, as we shall see, the second term is complex conjugate of the first and ε is thus real. We will therefore now introduce this spin-orbit coupling and recall some of its properties.

2.2.2 The spin-orbit interaction

The corresponding Hamiltonian is written:

$$H^{SO} = -\frac{e\hbar}{4m_e^2c^2}\{\sum_{i,\alpha}\overrightarrow{\sigma_i}.(\overrightarrow{E_\alpha}(\overrightarrow{r_{i\alpha}})\times\overrightarrow{p_i}) - \sum_{i\neq j}\overrightarrow{\sigma_i}.(\overrightarrow{E_j}(\overrightarrow{r_{ij}})\times(\overrightarrow{p_i}-2\overrightarrow{p_j})\} \quad (24)$$

where in the first term $\overrightarrow{E_\alpha}(\overrightarrow{r_{i\alpha}})\times\overrightarrow{p_i}/m_ec^2$ is a motional magnetic field corresponding to an electric field created by the nucleus α and seen by the electron i (neglecting the motion of the nucleus) and where the second term is the spin-other orbit interaction in which the motional magnetic field is created by the other electrons $j \neq i$.

An important approximation made by all authors this far, is to assume that the electric field seen by each electron can be replaced by an effective spherically symmetric field around each nucleus α:

$$\overrightarrow{E_\alpha}(\overrightarrow{r_{i\alpha}}) = -\frac{\overrightarrow{r_{i\alpha}}}{r_{i\alpha}}\frac{dV_\alpha(r_{i\alpha})}{dr_{i\alpha}} = \frac{Z_\alpha e}{4\pi\varepsilon_0}\frac{\overrightarrow{r_{i\alpha}}}{r_{i\alpha}}\frac{d}{dr_{i\alpha}}\left(\frac{1}{r_{i\alpha}}U\left(r_{i\alpha}\right)\right) \quad (25)$$

$$H^{SO} = \frac{\alpha^2}{4}\left(\alpha^2 m_e c^2\right)\sum_{i,\alpha}Z_\alpha\left(\frac{a_0}{r_{i\alpha}}\right)^3\left(U - r_{i\alpha}\frac{dU}{dr_{i\alpha}}\right)\overrightarrow{\sigma_i}.\overrightarrow{l_{i\alpha}} = \sum_{i,\alpha}a_\alpha(r_{i\alpha})\overrightarrow{s_i}.\overrightarrow{l_{i\alpha}} \quad (26)$$

where $\overrightarrow{l_{i\alpha}} = (\overrightarrow{r_{i\alpha}}\times\overrightarrow{p_i})/\hbar$ is the dimensionless orbital angular momentum of electron i around the nucleus α and $a_\alpha(r_{i\alpha})$ is the spin-orbit coupling parameter of the atom α:

$$a_\alpha(r_{i\alpha}) = \alpha^2 Z_\alpha\left(\frac{a_0}{r_{i\alpha}}\right)^3\left(U - r_{i\alpha}\frac{dU}{dr_{i\alpha}}\right)Ry \quad (27)$$

For atoms the matrix elements, that we will need later on, are given by :

$$\langle np_x\left|a(r)l_z\right|n'p_y\rangle = -i\int_0^{+\infty}a(r)R_{np}(r)R_{n'p}(r)r^2dr \quad (28)$$

and the diagonal elements of the spin-orbit Hamiltonian in the coupled basis $|\,(ls)jm\rangle$ are [54]:

$$\Delta E_{jlm}^{SO} = \left\langle n(ls)jm\left|H^{SO}\right|n(ls)jm\right\rangle = \zeta_{nl}\left[j(j+1) - l(l+1) - s(s+1)\right]/2 \quad (29)$$

with

$$\zeta_{nl} = \int_0^{+\infty}a(r)R_{nl}^2(r)r^2dr \quad (30)$$

In the case of a multielectron atom:

$$\zeta_{nl} = \alpha^2 \frac{Z_\alpha^2 H_r(lZ_\alpha)}{n_*^3 l(l+1)(l+1/2)} Ry \tag{31}$$

where Z_α is an effective charge and where H_r is a relativistic correction given in [54].

If we combine formulas 20 and 31 to estimate the order of magnitude of ΔE^{PV} in 23, we see that if $E_0 - E_n \approx 1$ Hartree then:

$$\Delta E^{PV} \sim \left(\frac{G_F m_e^2 c}{\hbar^3}\right) \alpha^4 \mathbf{Z}^4 \mathbf{Q}_W Ry \sim 8.5\ 10^{-21} \mathbf{Z}^5 \text{ Hartree} \tag{32}$$

Further theoretical work by Zel'dovich et al.[25], Harris and Stodolsky [28], Rein et al.[27], I.B. Khriplovich [29] introduce a multiplicative asymmetry factor η to include the effect of the molecular environment. Now, the whole problem is to calculate this asymmetry factor from basic principles, i.e. from formula 23 and from the molecular orbital theory.

2.3 Quantum chemistry calculations

The second important approximation made by Hegstrom, Rein and Sandars[27,51] to simplify the problem is to assume that the electronic wave functions can be written as a single Slater determinant: for closed shell molecules (with an even number $2N$ of electrons), the ground state wave function is approximated by a determinant of one-electron orthonormal orbitals φ_i each associated with spin functions $\chi_i = \alpha, \beta$:

$$\psi_0 = \frac{1}{\sqrt{(2N)!}} \begin{vmatrix} \varphi_1(1)\alpha(1) & \varphi_1(1)\beta(1) & \varphi_2(1)\alpha(1) & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\ \varphi_1(2)\alpha(2) & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots \\ \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots & \varphi_N(2N)\beta(2N) \end{vmatrix} \tag{33}$$

which can be written symbolically as $\psi_0 = \det\{\varphi_1\widetilde{\varphi}_1\varphi_2\widetilde{\varphi}_2.....\varphi_N\widetilde{\varphi}_N\}$ (the normalization factor is left out for simplicity in this short notation).

In addition to the N occupied orbitals $\varphi_i = \varphi_1, ...\varphi_N$, there are unoccupied molecular orbitals $\varphi_n = \varphi_{N+1}, \varphi_{N+2}...$ which can be used to construct approximate wave functions for excited states. The only ones, that we need to

consider here, are those obtained by the excitation of a single electron from an occupied molecular orbital φ_i to an unoccupied one φ_n. For each excitation, there are four such states, resulting in one singlet and one triplet:

$$\begin{aligned}\psi_{i\to n}^{(1)} &= [\det\{\varphi_1\widetilde{\varphi}_1.....\varphi_i\widetilde{\varphi}_n.....\} + \det\{\varphi_1\widetilde{\varphi}_1.....\varphi_n\widetilde{\varphi}_i.....\}]/\sqrt{2} \\ \psi_{i\to n}^{(3)} &= \left\{\begin{array}{l}\det\{\varphi_1\widetilde{\varphi}_1.....\widetilde{\varphi}_i\widetilde{\varphi}_n.....\} \\ [\det\{\varphi_1\widetilde{\varphi}_1.....\varphi_i\widetilde{\varphi}_n.....\} - \det\{\varphi_1\widetilde{\varphi}_1.....\varphi_n\widetilde{\varphi}_i.....\}]/\sqrt{2} \\ \det\{\varphi_1\widetilde{\varphi}_1.....\varphi_i\varphi_n.....\}\end{array}\right\} \end{aligned} \quad (34)$$

with excitation energies $E_{i\to n}^{(1)} - E_0$ and $E_{i\to n}^{(3)} - E_0$. Only the excited triplet states can be mixed with the ground state by the Hamiltonians that we consider here.

Since it involves only monoelectronic operators, formula 23 can then be applied to molecular orbitals by interpreting the E_n as orbital energies and ψ_n as molecular spin orbitals:

$$\Delta E_{el}^{PV} = \sum_i^{occ}\sum_n^{unocc} \frac{\left\langle \varphi_i\chi_i \left| H^{PV} \right| \varphi_n\chi_n \right\rangle \left\langle \varphi_n\chi_n \left| H^{SO} \right| \varphi_i\chi_i \right\rangle}{\varepsilon_i - \varepsilon_n} + c.c. \quad (35)$$

where i and n run respectively on the occupied and unoccupied orbitals of the ground state with energies ε_i and ε_n. The excitation energy $E_{i\to n}^{(3)} - E_0$ has been approximated by the difference of one-electron energies $\varepsilon_n - \varepsilon_i$, therefore neglecting the Coulomb interactions between electrons (for a better approximation see [44]).

Using

$$\left(\overrightarrow{\sigma}\cdot\overrightarrow{A}\right)\left(\overrightarrow{\sigma}\cdot\overrightarrow{B}\right) = \overrightarrow{A}\cdot\overrightarrow{B} + i\overrightarrow{\sigma}\cdot\overrightarrow{A}\times\overrightarrow{B} \quad (36)$$

$$\begin{aligned}\Delta E_{el}^{PV} = \frac{1}{2\sqrt{2}}\left(\frac{G_F m_e^2 c}{\hbar^3}\alpha^2\right)(m_e c^2\alpha^2) \quad (37)\\ a_0^4 \sum_{i,n,\alpha,\beta} \mathbf{Q}_W^\alpha \frac{\left\langle \varphi_i \left| \left\{\overrightarrow{p}/\hbar, \delta^{(3)}(\overrightarrow{r_\alpha})\right\}_+ \right| \varphi_n \right\rangle \cdot \left\langle \varphi_n \left| a_\beta(r_\beta)\overrightarrow{l_\beta} \right| \varphi_i \right\rangle}{\varepsilon_i - \varepsilon_n}\end{aligned}$$

where $\overrightarrow{r_\alpha}$ stands for $\overrightarrow{r} - \overrightarrow{r_\alpha}$.

The similarity between this expression and the corresponding one giving optical rotation has been emphasized [27]. In many aspects, this calculation is also quite similar to the calculation of the molecular Zeeman effect or to the calculation of hyperfine coupling constants.

The LCAO approach, in which, molecular orbitals are expanded on a basis of real atomic orbitals is then generally adopted:

$$|\varphi_i\rangle = \sum_{\alpha,\gamma} c_{i\gamma}^{\alpha} |\varphi_{\gamma}^{\alpha}\rangle \tag{38}$$

which gives finally:

$$\begin{aligned} \Delta E_{el}^{PV} = & \frac{1}{2\sqrt{2}} \left(\frac{G_F m_e^2 c}{\hbar^3} \alpha^2 \right) (m_e c^2 \alpha^2) \\ & a_0^4/\hbar \sum_{\substack{i,e \\ \alpha,\beta,\gamma,...}} c_{i\gamma}^{\alpha} c_{e\gamma'}^{\alpha} c_{e\gamma''}^{\beta} c_{i\gamma'''}^{\beta} \mathbf{Q}_W^{\alpha} \\ & \langle \varphi_{\gamma}^{\alpha} | \left\{ \overrightarrow{p}, \delta^{(3)}(\overrightarrow{r_{\alpha}}) \right\}_+ | \varphi_{\gamma'}^{\alpha} \rangle \\ & \langle \varphi_{\gamma''}^{\beta} | a_{\beta}(r_{\beta}) \overrightarrow{l_{\beta}} | \varphi_{\gamma'''}^{\beta} \rangle \\ & (\varepsilon_i - \varepsilon_e)^{-1} \end{aligned} \tag{39}$$

To write this formula, a simplification has been made, which consists in restricting each matrix element to a single center, therefore neglecting the overlap: the same nucleus α or β is selected for the atomic orbitals and for the interaction.

It was shown, by Hegstrom, Rein and Sandars [51] that, in this formula, the one-center terms ($\alpha = \beta$) are much smaller and vanish for a pure and single *sp* basis set. This is what they called the single center theorem: $\alpha \neq \beta$. As a consequence, the parity-violating terms will be proportional to $\mathbf{Z}_{\alpha}^3 \mathbf{Z}_{\beta}^2$ for each pair of nuclei.

Also, one can understand that if a given nucleus α has a symmetric environment, terms corresponding to partners $\beta, \beta', ..$symmetrically located will cancel each other since they will change signs by mirror reflection.

The total energy shift ΔE_{el}^{PV} is then a sum of separate contributions $\Delta E_{el}^{PV}(\alpha)$ from each of the nuclei composing the molecule.

Using this theoretical approach, Hegstrom, Rein and Sandars have performed the first ab initio molecular orbital calculation of the parity violating energy shift of an enantiomer, the (R) isomer of the chiral ethylene-2 [51] for which they found $\eta = 3.10^{-4}$.

Following the work of Hegstrom, Rein and Sandars, this ab initio approach based on MO/LCAO was applied to a number of molecules, especially by Mason, Tranter, MacDermott and co-workers [42,43,44,55−66], using the GAUSSIAN program to construct Slater type orbitals from a number of Gaussian functions. They studied H_2O_2 , L-alanine for which $\Delta E_{el}^{PV} \sim 10^{-20} a.u.$ [55]; for H_2O_2 [55],

L-alanine [55,56] and L-peptides [56] they performed studies vs dihedral angle. For H_2S_2 [57]the ratio of the effect to that in H_2O_2 is ~ 500 which is larger than the Z^5 ratio equal to 32; studies of the L-α-amino acids, specifically the L-alanine and the glycine yield $\Delta E_{el}^{PV} \sim -10^{-20} a.u.$ [57] which means that the L-series are preferentially stabilized by the electroweak interaction; this was confirmed on the series: glycine, alanine, valine, serine, aspartic acid $\Delta E_{el}^{PV} \sim -0.84$ to$-2.29\ 10^{-20} a.u.$ [44]. Similar results on the D-Sugar series gave some credit to the speculations about biochemistry.

The most recent calculations confirm a large enhancement (3 orders of magnitude) when carbon is replaced by sulfur [65]. As another example, L.Ivanov and V. Letokhov [67] have considered hypothetical four-atom molecules such as NFClBr, BiFClBr, and NFClAt, for which the calculated ΔE_{el}^{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. These authors also point out the importance of relativistic effects for the electron wave function in the nuclei vicinity, which could be a major source of error in the previous approach.

2.4 Letokhov's conjecture [24]

The difference between electronic energies of enantiomers is very difficult to detect directly since it comes on top of the rest mass energy of the molecule. The only consequence that we might expect is a slight difference in Boltzmann factors for the populations or in reaction rates leading to a preference in the chemical formation of one of the two species (one should emphasize that a number of kinetic dissymmetry amplification mechanisms have been suggested, such as the Kondepudi catastrophic bifurcation mechanism [68], or the Yamagata cumulative amplification mechanism [69]). If we want to probe the difference by means of spectroscopy, it is necessary to estimate a possible difference in the spectra, that is a difference between the parity-violating energy differences in the two levels involved in the transition. As is well-known, in molecular spectroscopy, we may have electronic, vibrational or rotational degrees of freedom. There is a general relationship between the energies associated with these three degrees of freedom [70] :

$$\begin{aligned} E_{vib} &\approx \left(\frac{m_e}{M}\right)^{1/2} E_{el} \Longrightarrow \Delta E_{vib} \approx \left(\frac{m_e}{M}\right)^{1/2} \Delta E_{el} \\ E_{rot} &\approx \left(\frac{m_e}{M}\right) E_{el} \Longrightarrow \Delta E_{rot} \approx \left(\frac{m_e}{M}\right) \Delta E_{el} \end{aligned} \tag{40}$$

where M is of the order of an atomic mass. So that 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:

$$\frac{\Delta E_{el}}{E_{el}} \approx \frac{\Delta E_{vib}}{E_{vib}} \approx \frac{\Delta E_{rot}}{E_{rot}} \tag{41}$$

This argument is based on a global and rather indirect relationship and needs to be refined to be fully credible, because it is not the overall electronic energy which is directly related to the vibrational frequency, but rather its second-derivative with respect to the internuclear distances. In fact, $\Delta E_{el}^{PV}(\overrightarrow{r_\alpha})$ acts as a PV-potential between the nuclei. It depends explicitly on the nuclear coordinates corresponding to the vibration modes of the molecule. A detailed calculation of the expansion of ΔE_{el}^{PV} in normal coordinates will be presented in a forthcoming paper. If x_i are the deviations about the parity-conserving equilibrium:

$$\Delta E_{el}^{PV}(x) = \alpha + \sum_i \beta_i x_i + \frac{1}{2}\sum_{ij} \gamma_{ij} x_i x_j \tag{42}$$

The coefficients β will be responsible for a slight difference in equilibrium geometries between the enantiomers and it has been argued that, the electromagnetic interactions being then different, this might cancel the parity-violating energy difference between the two forms. This effect has been estimated by G.E. Tranter to be of the order of 10^{-60} and hence negligible [59].

The coefficients γ in the expansion give the difference in force constants C and hence a difference $\approx \pm\nu\gamma/2C$ of vibration frequency between the enantiomers. With a typical force constant of the order of 1 a.u.(angstrom)$^{-2}$ and an order of magnitude [43] for the value of the parity-violating force constant in organic compounds (without heavier atom than carbon) equal to 10^{-20}a.u.(angstrom)$^{-2}$, one obtains $\Delta\nu/\nu \sim 10^{-20}$. We see that the $\mathbf{Z}_\alpha^3\mathbf{Z}_\beta^2$ dependence and the associated relativistic factors will be essential to bring this value to a reasonable level.

3 Experimental test using nonlinear spectroscopy

3.1 Historical background

Although the theoretical work on parity violation in chiral molecules has been quite intense and regular over the past twenty years, the experimental efforts have been more modest, mainly because such a project appeared to be a very difficult challenge involving both physics and chemistry. The first challenge

concerned our ability to compare the energies of two molecules with a very high accuracy. As stated previously, only energy differences can be measured with sufficiently high accuracy, thanks to the developments of new methods in modern nonlinear spectroscopy. These methods use combinations of several light waves either copropagating or counterpropagating, to get rid of the Doppler broadening and obtain extremely narrow resonances. With one of these techniques, called saturation spectroscopy [71−78], it is now possible to reach resolving powers in the 10^{11} range and linewidths less than 100 Hz in almost any part of the spectrum from microwaves to near U.V.. Furthermore, these very narrow resonances may be used as error signals to lock a laser frequency to their line center with unprecedented stabilities, reproducibilities and accuracies. The sensitivity of an experiment performed with the racemic mixture is limited by the resolution of the spectrometer. If it is possible to resolve the two enantiomers, it is possible to perform a beat experiment or to record simultaneously the spectra of the two species as we have preferred to do in the present work. The sensitivity in that case, will be limited by the precision with which the line center is determined, which is usually more precise than the limitation imposed by the resolution by several orders of magnitude.

The next challenge was to find a relevant molecule for such a test. In 1976, Letokhov and coll. [79] suggested that CHFClBr, as a chiral molecule, would be a good candidate for an observation of parity violation. They obtained a few saturation resonances of the racemic mixture of CHFClBr with a typical resolution of the order of 1 MHz but no obvious splitting could be observed. During the years 1977-1978, these experiments were repeated in our laboratory with a higher resolution (typically 50 to 100 kHz corresponding to free-running lasers) both on CHFClBr and CHFClI with the same conclusion. Experiments with resolved enantiomers of CHFClCOOH failed to exhibit any saturation resonance with the spectrometer used at that time and this effort was stopped until recently when resolved enantiomers of CHFClBr became available. We should also mention the paper of Arimondo et al. [80] where a beat experiment is reported with the enantiomers of camphor with a sensitivity of 10^{-8}, far from the requirements estimated by theory, and obvious interpretation problems given the complexity of this molecule.

Today CHFClBr is certainly one of the best molecules for such a project for different reasons : in the ground vibronic state the inversion is negligible and hence the enantiomers are stable; it contains a bromine atom with a high Z value ($Z_{Br} = 35$), located at the molecule periphery; the number of atoms is limited, which results in a moderate partition function and hence reasonable populations in each state; the vapor pressure is high at room temperature. Likely the enantiomers of CHFClI can also be resolved in the near future and

it would be an even better candidate because Z_I=53 but the experimental and theoretical spectroscopic data on CHFClBr are, up to now, much more extensive. In particular, the strong ν_4 CF stretching fundamental has been fully analyzed [81,82,83]. The knowledge of this vibration band, which matches the R branch of the 9.4 μm CO_2 laser band, is a necessary starting point for any ultra-high resolution experiment at that wavelength. Finally a number of studies of the vibrational circular dichroism have been performed [85,86].

Any experimental project was withheld over twenty years because the final difficulty of the resolution of CHFClBr enantiomers was solved successfully only recently [87]. The link between the conformation and the optical activity of the two isomers of CHFClBr was established even more recently by the group of A. Collet [88,89,90] S-(+) and R-(-). This group provided us with one sample of R-CHFClBr with an enantiomeric excess (ee) of 22±2 % and one sample of S-CHFClBr with an ee of 56,5±0,5 %. This has enabled us to try to perform a test of parity violation in molecules with a sensitivity, which is, for the first time, compatible with the expected effect.

3.2 Experimental set-up

The principle of the experiment is the following : we use a single CO_2 laser whose frequency is stabilized on a saturation peak detected in the transmission signal of a 1.5 m long Fabry-Perot resonator. The frequency stabilization scheme is described in more detail elsewhere [91]. It can provide a spectral purity of 6 Hz and a long-term stability of 0.1 Hz over 100 s. These performances have been achieved in the 10 μm spectral region with a strong OsO_4 saturation resonance. In the present experiment, we have operated on the R(14) CO_2 laser line of the 9.4 μm band. We have used a sample of racemic CHFClBr and we have chosen one strong hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ rovibrational line as the reference line to stabilize the laser frequency. At that wavelength, the finesse of the cavity was degraded by a factor 2 (finesse of only 100) and the line was about 10 times broader than for OsO_4. As a consequence, we have estimated the spectral width of the laser to be about 100 Hz, which is not presently a limitation of the experiment. For the same reason, the long-term stability is also degraded but, as we shall see, a drift of the laser frequency has no impact on the sensitivity of the test, as far as the drift is much less than the width of the molecular lines involved in the left-right comparison.

In a first scheme, the laser frequency feeds an electro-optic modulator (EOM) which generates sidebands between 8 and 18 GHz on each side of the laser carrier, which is frequency-stabilized. The power in each sideband is about 10^{-4} of the power in the carrier but the crossed polarizations of the

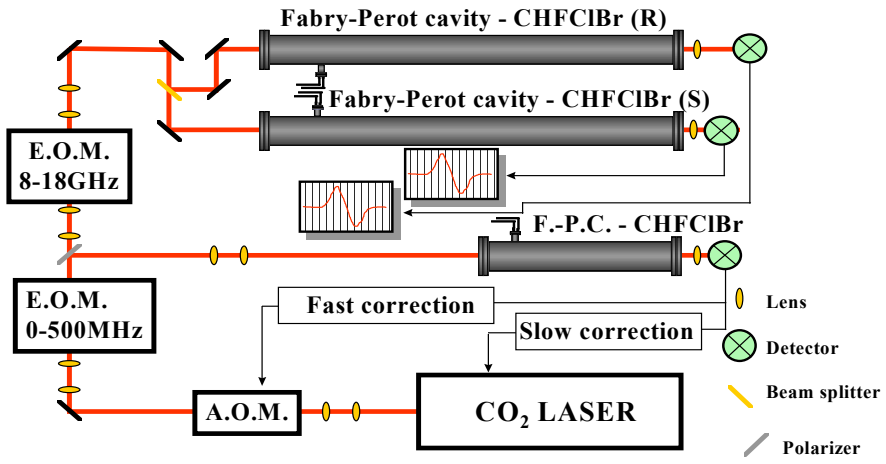

Figure 3: Schematic diagram of the experimental set-up

carrier and of the sidebands result in a quite effective rejection of the carrier. One of these sidebands feeds two twin 3 meter long Fabry-Perot resonators (cavities), whose resonance frequencies are slaved to this sideband frequency. Each of these cavities is filled by one of the enantiomers of CHFClBr. By tuning the EOM, we tune the sideband frequency and we can record simultaneously the spectra of the two enantiomers. Through a fit of both spectra, we obtain two line centers measured relative to the frequency of the stabilized laser carrier. Thus, any drift of this carrier frequency cancels in the difference between the two line centers. This represents an elementary measurement of the parity violation effect.

After several attempts to optimize this scheme on the (27,9,18)← (27,10,17) line located at -14,4 GHz from the R(14) laser line, we have faced several difficulties : the finesse of the cavities has dropped from 200 down to 100 for the 1.5 m long resonator and from 170 to 50 for the 3 m long resonators as the spectrometer was tuned from the 10,6 μm to the 9,4 μm spectral region. We were able to resolve partially very rich hyperfine structures but the ultimate resolution was still limited by an unresolved hyperfine structure. Thus, the optimum signal was obtained at a relatively high pressure, for which the collisional broadening was dominant. In these conditions, the power available in the sideband was not sufficient to saturate efficiently the molecular transitions. Thus, we decided to adapt this scheme in the following manner: we kept the stabilization system in which the laser carrier operates at a frequency shifted

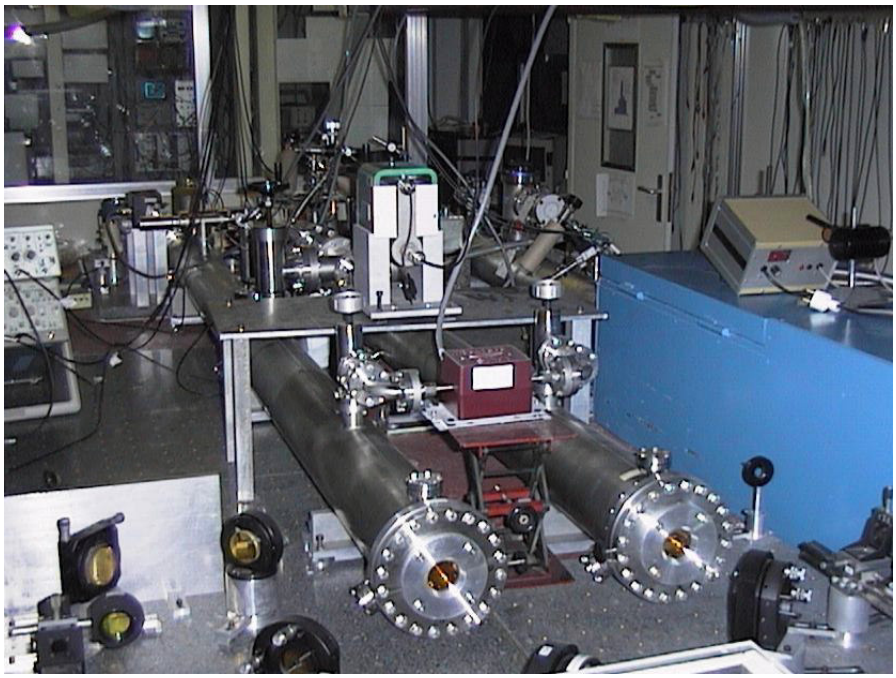

Figure 4: View of the experiment showing the two Fabry-Perot resonators

from the molecular resonance by the radiofrequency of the 0-500 MHz EOM. Then, the carrier, shifted by an acousto-optic modulator for an optical isolation purpose, fed directly the twin cavities without using the 8-18 GHz EOM, and the recording of the spectra of the two enantiomers was achieved by tuning the radiofrequency of the first EOM. With this scheme, we had enough power to saturate the transitions but we lost the broadband tunability provided by the 8-18 GHz EOM and we were limited by the coincidences between the CO_2 laser lines and the spectrum of CHFClBr. The frequency modulations required to stabilize the resonators and to detect the molecular signals in transmission of these three cavities could not be applied to the EOMs. Thus, we applied two modulations directly inside the laser resonator via a piezoelectric transducer, one at 45 kHz was used to stabilize the optical length of the three cavities and the second one at 12 kHz was used with a third-harmonic detection to stabilize the sideband on a molecular signal and to detect the molecular resonances of the two enantiomers. The modulation parameters were optimized for the

signals in the twin cavities. This induced a slight degradation of the stability of the laser with no measurable effect on the sensitivity of the present experiment. Finally we performed the most sensitive experiments through a study of one hyperfine component of the $(40, 7, 34) \leftarrow (40, 8, 33)$ rovibrational line, while a different hyperfine component was used for the frequency stabilization. By recording the same hyperfine component in a very large cell (18 m long with an 8 cm laser beam diameter) with a resolution of 5 kHz, one can see on figure 5 that the selected line appears to be a symmetric triplet. This explains why we could not obtain a resolution better than 90 kHz in the Fabry-Perot cavity.

The difficulty of this experiment is to reduce the systematic effects in these measurements as much as possible. With this respect, the fact that the spectral properties of the laser light, which feeds the two resonators is identical is certainly very helpful. Actually, any difference in the experimental environment of the two compared enantiomers is generated from the beamsplitter which divides the laser beam in two parts directed towards the two cavities. We can try to list the parameters which could be different for the two samples:

- light polarization: we wanted to have a linear polarization in order to avoid any chirality external to the molecules. A slight discrepancy from the linear polarization of the sideband can induce some ellipticity after the beamsplitter. We estimate to control the linearity within one degree. Furthermore, the residual light chirality is strongly attenuated (by the finesse) inside the Fabry-Perot resonator since a $\sigma+$ polarization relative to the propagation axis is converted into $\sigma-$ after each reflection.

- the mode matching into the two resonators depends on the alignment of the two cavities and the adjustment of the path lengths between the beam splitter and the cavities.

- the finesse of the two cavities which depends on the reflectivity and on the losses of the mirrors.

- the laser power inside the resonators.

- the mode profile of the beam inside each resonator, which depends on the radii of curvature of the mirrors and affects the interaction time of the molecules with the light.

- the pressure in the Fabry-Perot cavities.

- the residual stray fields : the magnetic shielding in the cavities reduces the earth magnetic field by three orders of magnitude.

- the constitution of the samples : impurities can induce various collisional shifts. In particular, in each sample, two kinds of collisions can occur : "homocollisions" R-R and S-S and "heterocollisions" R-S which might give a different collisional shift. Since the enantiomeric excesses are different, we can

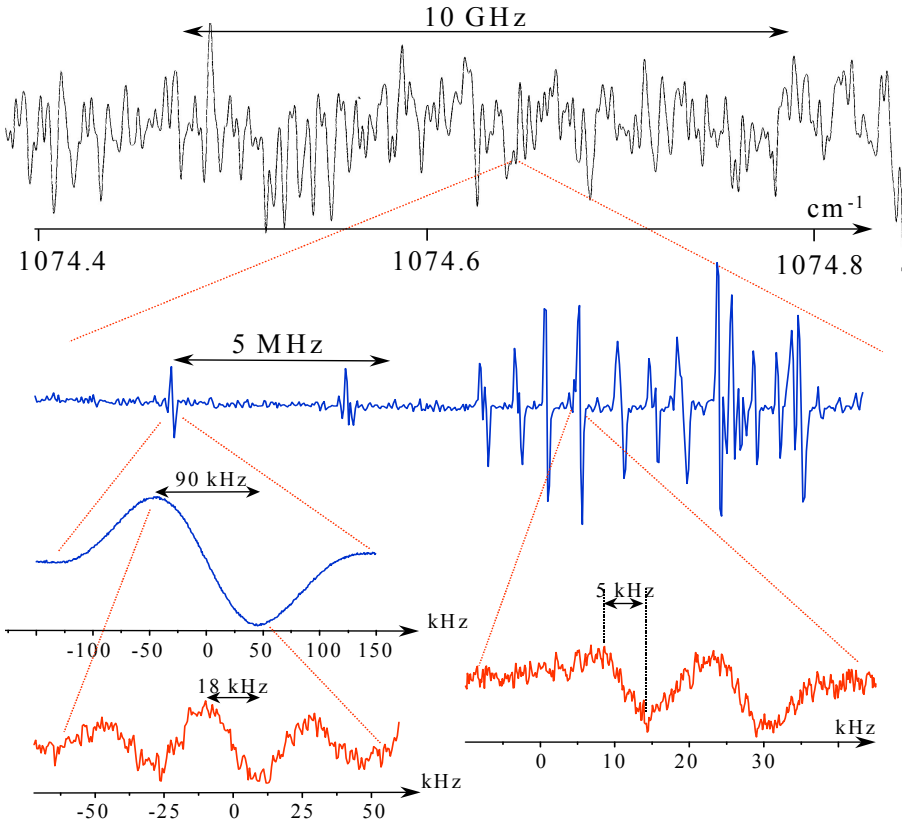

Figure 5: Spectra of CHFClBr around 1074.6 cm^{-1} for increasing resolving powers. From top to bottom: Fourier transform spectrum, saturation spectrum with a free-running CO_2 laser exhibiting the full hyperfine structure of the line, frequency-controlled saturation spectrum of a single resonance in the twin Fabry-Perot resonators revealing its structure with the large cell.

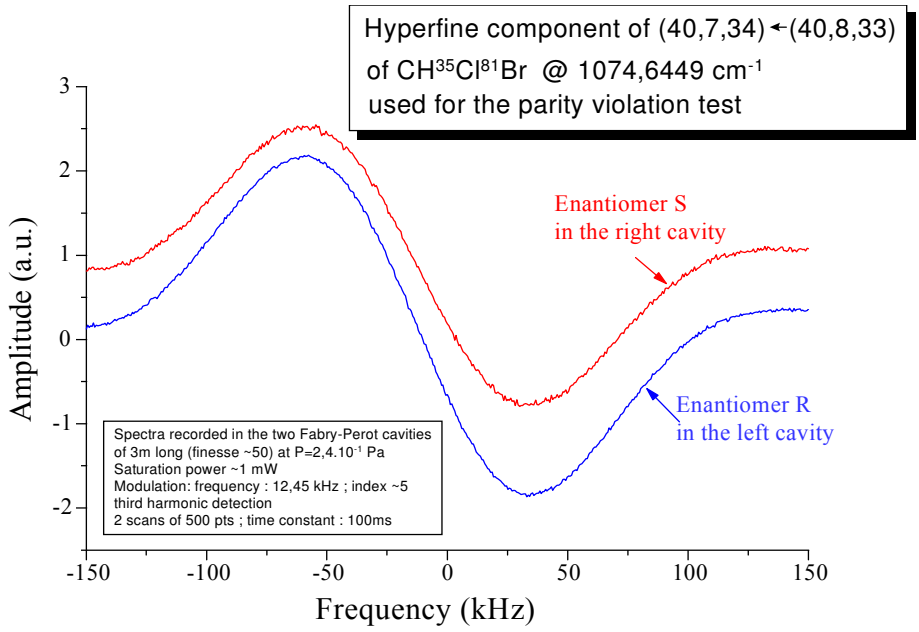

Figure 6: Saturation resonances recorded simultaneously for enantiomorphic species in their respective Fabry-Perot resonator.

obtain an irreducible frequency difference whose signature would be a pressure dependence.

- the sensitivity of the photodetectors after the cavities.
- the alignment on the detectors.

Most of the differences between the two systems (in addition to the enantiomorphic molecules themselves) are compensated by the exchange of the role of the two cavities performed by filling the cavities with the other enantiomer. However, this is not the case for the polarization effects and the stray fields. By changing the polarization of the laser light, it was not possible to see any influence on the line center determinations. Although we have no data about the influence of a magnetic field on the spectrum of CHFClBr, recent measurements on OsO_4 revealed a typical dependence of about 1 Hz/G. This would be negligible at the present level of sensitivity, if the value was similar for CHFClBr, which has still to be investigated.

The results that we present now, correspond to 10 sets of measurements performed over 10 days. For one set per day, the first half-day, each twin

cavity is filled with one kind of enantiomer and the second part of the day, the enantiomers are exchanged in the cavities. When we perform an elementary measurement as described above, we usually obtain a systematic shift of the order of 100 Hz which is reproducible. When the role of the cavities are exchanged, we observe that the sign of the difference is changed (see Figure 7(top)). This systematic effect can be associated with the difference between the two systems and, by assuming that this shift is constant over one day, we can calculate its average value and substract it from the individual measurements. This is illustrated on Figure 7(bottom) which shows a white distribution of data close to zero.

The systematic shift, that we eliminate by the preceeding procedure, has an unknown physical origin. Several mechanisms can be responsible for these shifts:

- two different saturation parameters in the twin cavities can induce different light shifts and differential saturations of the unresolved hyperfine components [72], especially if the studied line includes crossover resonances.

- a gas lens effect in the resonators [77,78], an effect for which there is no good strong field theory and which is sensitive to the diaphragms at the input and output of the cavities.

This shift cannot be very easily studied experimentally, because it is of the same order of magnitude as the precision of the individual measurements. However, it is quite stable over one day as revealed by the compensation procedure. It depends certainly on the alignment conditions since the shift is not reproducible from one day to another.

Once this compensation was achieved, we could build the histogram from the 580 individual corrected measurements, which is well fitted by a Gaussian. We obtain a mean value for the frequency difference of $3,7$ Hz and a standard deviation of $47,2$ Hz which is very close to the typical uncertainty given by the fit of the spectra.

The global precision 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. This is true if we consider only the statistical errors. However, systematic effects are present in this experiment. Although the compensation seemed to be effective, we cannot claim that it is perfect. Some residual and uncontrolled effects are persistent and must be taken into acount in the uncertainty of the final result.

We estimate that these residual systematic effects are of the order of 5 Hz. Thus, the frequency difference for the resonances associated to the two samples is:

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

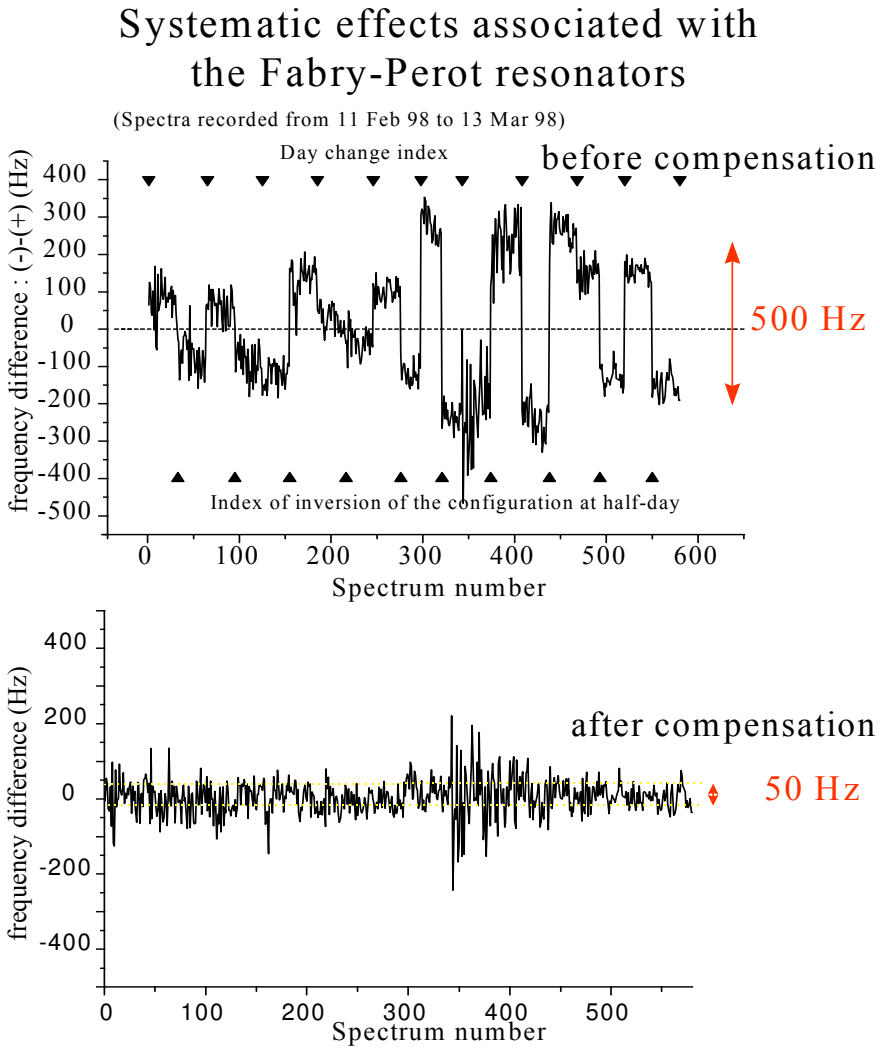

Figure 7: Compensation of the systematic errors by an exchange of the roles of the two resonators

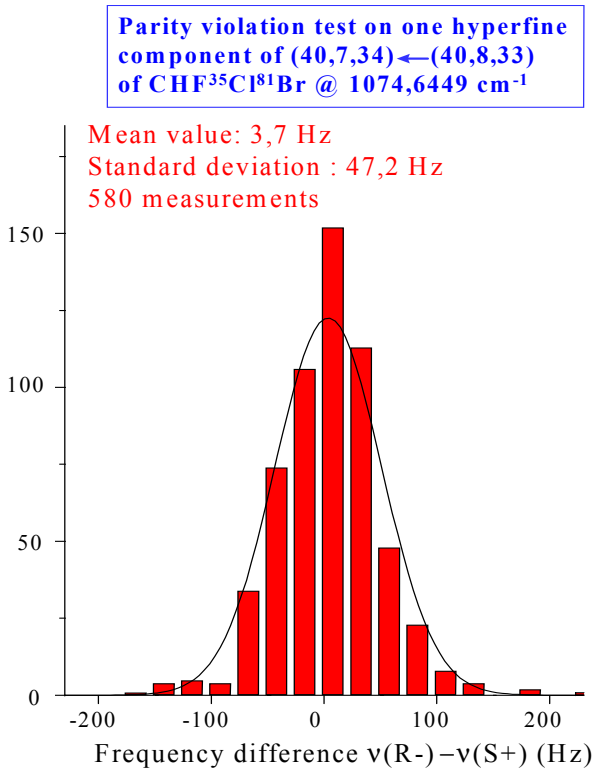

Figure 8: Histogram of the measured frequency differences for 580 measurements

In order to give the actual frequency difference for the two enantiomers, we have to take into account the enantiomeric excesses of the samples. We finally obtain the first test of parity violation on the CHFClBr molecule:

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

This result is negative. It gives an upper limit of $\Delta\nu/\nu \simeq 3,9.10^{-13}$ for the effect.

4 Conclusion and directions of future work

The sensitivity achieved in this experiment is about five orders of magnitude higher than the previous similar test on camphor and than the upper bound inferred from the spectra of racemic CHFClBr and CHFClI. This experiment

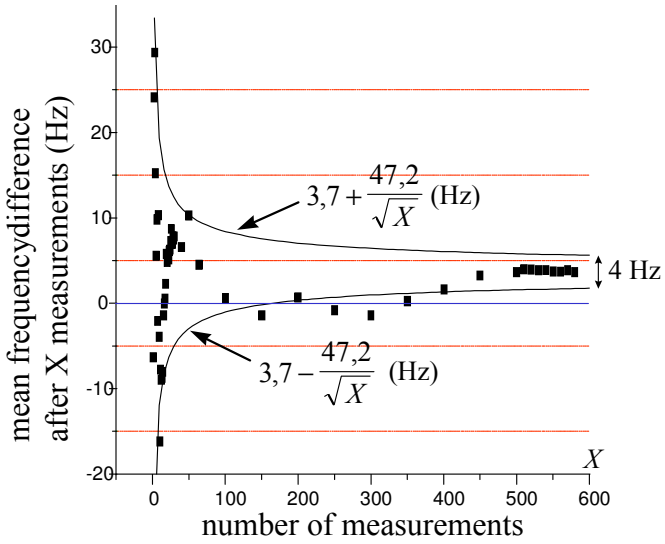

Figure 9: Convergence of the average value of the measured frequency differences ν(R-)-ν(S+) after X measurements.

is still to be considered as a preliminary test and there is clearly a lot of possibilities to improve its sensitivity. On a short term time scale, we can certainly make a better choice of line (we suspect that the resonance, which was used for these first experiments, was in fact a crossover resonance, more sensitive to light shifts than the main lines). An optimized choice will eventually require the detailed analysis of the hyperfine structure in the spectrum of CHFClBr. We can already use higher finesse Fabry-Perot resonators, a higher enantiomorphic excess (up to 80% is available now from A. Collet and J. Costante), a better control of the sample purity, of the total pressure and more generally a better understanding of systematics of our present experiment. Later we can reduce these systematic errors with a higher resolution using beams of larger diameter or possibly slow molecules[76]. New experiments are already in progress with our high resolution spectrometer using a large cell. Unfortunately this cell is presently unique and experiments with enantiomers would have to be done in a sequential mode (the required frequency stability of the laser would then be provided by a Fabry-Perot device such as those described in this paper).

We may reasonably hope to improve our sensitivity by at least two orders of magnitude in the next few years. On a longer term time scale, future

experiments may use saturation spectroscopy in molecular beams to avoid any collisional shift combined with molecular interferometry [50], molecules with heavier atoms like CHFClI and more sensitive transitions: CBr or CI vibrations. Finally, it is already clear now that the theory is insufficiently developed to get a reliable estimate of the expected effect in various molecules and has to be improved substantially.

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