Simultaneous Enantiomer-Resolved Ramsey Spectroscopy for Chiral Molecules

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We introduce a scheme to perform Ramsey spectroscopy on a racemic mixture of chiral molecules, simultaneously extracting the transition frequencies of the left- and right-handed molecules, known as enantiomers. By taking the difference between the enantiomeric frequencies, we isolate the weak force parity violation (PV) shift, which is predicted to break the symmetry between enantiomers. Ramsey interrogation of the two transitions is implemented by creating enantiomeric superpositions in a three level system using the enantiomer-dependent sign of the dipole moments. Our technique overcomes the need to alternate between enantio-pure samples to measure PV. We describe the advantages of the proposed method for precision metrology. The challenge of measuring $\Delta_{PV}^{vb}$ lies in its tiny magnitude, where estimations for organic chiral molecules such as CHBrClF are smaller than 10 mHz [7]. However, calculations predict that $\Delta_{PV}^{vb}$ can be enhanced by two orders of magnitude for electronically excited states, due to the reduced cancellation of PV contributions from different orbitals [15]. An alternative approach to increase the effect utilizes substitution of heavy metal nuclei in the molecule [10, 20]. In N=UHF for example, $\Delta_{PV}^{vb}$ is calculated to rise to the order of 10 Hz [20]. Multiple techniques have been used and proposed to measure PV in chiral molecules including Fourier transform infrared (FTIR) spectroscopy [21, 23], microwave spectroscopy [21], vibrational Ramsey spectroscopy [25], NMR spectroscopy [29] and matter-wave interferometry [27]. In these techniques, the ability to synthesize enantiomer-enriched samples has been described as a key requirement [21, 28, 29]. However, realizing this requirement is difficult for the molecules that are particularly appealing for PV measurement. Here we show how to avoid this requirement.

Many methods exist for enantiomer enrichment with varying degrees of success [30]. One scheme, known as three-wave mixing, has particularly excellent prospects for efficient enrichment [31, 37]. Its principles form the foundation of our work. The scheme has been demonstrated to excite a sample of left ($L$) and right ($R$) handed molecules from an initial state $|1\rangle$ to either state $|2\rangle$ or $|3\rangle$ using the enantiomer-specific sign of the transition dipole moment.

Here we propose a fully differential scheme that leverages racemic enantiomer mixtures to directly extract the PV signature. Instead of comparing transitions in separate enanto-pure samples, we use an identical experimental sequence to simultaneously measure two transition frequencies in a racemic sample. This trait implies support for common-mode noise rejection for the difference between the transitions, with the statistical sensitivity likely approaching the Standard Quantum Limit (SQL) as demonstrated in ref. [38]. This makes our scheme particularly appealing for precision measurement. Finally, we introduce a framework of experimental switches that isolate the PV contribution.

For our scheme, we developed a pulse sequence to perform two Ramsey spectroscopies in a three-level system (Fig. 1). Each enantiomer is excited to a unique superposition using the sign difference between the scalar triple products of their transition dipole moment components: $\mu_x^L \cdot (\mu_y^L \times \mu_z^L) = -\mu_x^L \cdot (\mu_y^L \times \mu_z^L)$. Analogously to two-state Ramsey, a second excitation allows us to measure the energy difference of each superposition in separate final states. We apply the method to vibrational transitions where PV is enhanced throughout the rest of this work. However, the method could be applied to ongoing experiments with microwave rotational transitions for precision spectroscopy of PV [21, 30].

For our procedure, three states are coupled by fields along the P, Q and S transitions [Fig. 1(b)] with mutually orthogonal polarizations to interact with all 3 dipole components.
components. We set the phase relation of the fields to
\[ \Delta \phi = \phi_P - \phi_Q + \phi_S = \pm \pi/2 \] (1)
which is required to break the symmetry between states [2] and [3] in order to achieve perfect enantiomer separation [34]. The applied time-dependent interactions are
\[ \langle \vec{\mu} \cdot \vec{E} \rangle = 2\hbar \Omega_X \cos(\omega_X t + \phi_X), \] where \( X \in \{ P, Q, S \} \) and \( \Omega_X, \omega_X, \phi_X, \) and \( \delta_X \) denote the Rabi rate, frequency, phase, and detuning from the resonant transition of each field, as depicted in Fig. 1(b). Applying the rotating wave approximation (RWA), the Hamiltonian describing the interaction for multiple configurations is
\[
\frac{H_{\text{RWA}}}{\hbar} = \begin{pmatrix}
0 & \Omega_P & \Omega_Q \\
\Omega_P & \delta - \delta_S/2 + \bar{\kappa} \Delta_{P}^{\text{vib}} & \bar{\Phi} \bar{\kappa} e^{i \tau/2} \Omega_S \\
\Omega_Q & \bar{\Phi} \bar{\kappa} e^{-i \tau/2} \Omega_S & \delta + \delta_S/2 + \bar{\kappa} \Delta_{S}^{\text{vib}}
\end{pmatrix}
\] (2)
The Rabi rates \( \Omega_P, \Omega_Q \) and \( \Omega_S \) are time dependent and pulsed on individually [Fig. 1(c)]. We choose the detunings such that \( \delta_P - \delta_Q + \delta_S = 0 \) and use the convenient notation of the average vibrational detuning \( \bar{\delta} = (\delta_P + \delta_Q)/2 \). The handedness of the molecule is denoted by \( \bar{\kappa} \), where \( \bar{\kappa}(L) = -1 \) and \( \bar{\kappa}(R) = +1 \) such that the PV energy shift of an enantiomer is \( \bar{\kappa} \Delta_{P}^{\text{vib}} \). To model the sign change of the transition dipole moment, \( \bar{\kappa} \) is applied without loss of generality to the \( \bar{S} \) transition \( \bar{\kappa}(2)\mu \cdot \bar{E}[3] \) [34]. The sign of the relative phase [Eq. 1] is denoted by \( \Phi = \pm 1 \) using the relation \( e^{\pm i \tau/2} = \Phi e^{i \delta_X \tau} \).

Our scheme begins with both \( L \) and \( R \) enantiomers populating state [1]. Following Fig. 2(a) for the \( \Phi = -1 \) (\( \Delta \phi = -\pi/2 \)) case, the first \( \pi/2 \) pulse sequence creates the enantiomer-specific superposition states \( |L\rangle = (|1\rangle - i|2\rangle)/\sqrt{2} \) and \( |R\rangle = (|1\rangle - i|3\rangle)/\sqrt{2} \). After the molecules freely evolve for a duration \( \tau \), we apply the second \( \pi/2 \) pulse sequence to stop the phase evolution. The resulting populations in states [2] and [3] (\( \Sigma = -1, +1 \) respectively) as a function of \( \tau \) are depicted in Fig. 2(b) and given by the general equations
\[ N_{\Phi, \Sigma} = \frac{\bar{N}}{2} \left[ \cos \left( \delta_{\Phi, \Sigma} \tau \right) + 1 \right] \] (3)
\[ \delta_{\Phi, \Sigma} = \delta + \bar{\Sigma} \delta_S/2 - \bar{\Phi} \bar{\kappa} \Delta_{P}^{\text{vib}} \] (4)
where \( \bar{N} \) is the mean number of each enantiomer in the sample. We apply a realistic \( \Delta_{P}^{\text{vib}} = 10 \) Hz as calculated for N=UHF [20], which causes the slightly different frequencies for the populations of [2] and [3]. These two frequencies mix in [1] where the \( L \) and \( R \) populations beat.

The populations in states [2] and [3] can be measured by single-photon photo-dissociation of the molecule and separating the photo-fragments according to their kinetic energies, via velocity map imaging [39] for example [Fig. 1(d)]. If needed, the kinetic energy difference can be amplified by further excitation of the population in one of these states.

When the relative phase of the fields is switched to \( \Phi = +1 \) (\( \Delta \phi = \pi/2 \)), the roles of states [2] and [3] are
form frequency channels, which have intuitive physical (Fig. 3). The linear combinations of these switch-states \{\pm\text{encodes the chirality for a given configuration.} \}

The Ramsey sequence for a specific relative phase \(\tilde{\Phi}\) and \(\tilde{\Sigma}\) are given by Eq. (4), where \(\tilde{\Sigma}\) must be measured to complete a data block (Fig. 3). In this case, the superposition states formed in the Ramsey sequence are \(|L\rangle = (|1\rangle - i|3\rangle)/\sqrt{2}\) and \(|R\rangle = (|1\rangle - i|2\rangle)/\sqrt{2}\). The frequencies read out by the Ramsey sequence for a specific relative phase \(\tilde{\Phi}\) and state readout \(\tilde{\Sigma}\) are given by Eq. (1), where \(\tilde{\kappa} = -\tilde{\Phi} \cdot \tilde{\Sigma}\) encodes the chirality for a given configuration.

All four switch-states or configurations \(\{\tilde{\Phi}, \tilde{\Sigma}\} = \{\pm1, \pm1\}\) must be measured to complete a data block (Fig. 3). The linear combinations of these switch-states form frequency channels, which have intuitive physical meaning.

\[
2\pi \begin{pmatrix}
    f_0 \\
    f_\Phi \\
    f_\Sigma \\
    f_{\Phi \Sigma}
\end{pmatrix}
= \frac{1}{4} \begin{pmatrix}
    + & + & + & + \\
    + & + & + & + \\
    + & + & + & + \\
    + & + & + & +
\end{pmatrix}
\begin{pmatrix}
    \delta_{\Phi +, \Sigma^+} \\
    \delta_{\Phi +, \Sigma^-} \\
    \delta_{\Phi -, \Sigma^+} \\
    \delta_{\Phi -, \Sigma^-}
\end{pmatrix}
= \begin{pmatrix}
    \delta \\
    0 \\
    \delta_\Sigma/2 \\
    \Delta_{\text{ vib}}/\hbar
\end{pmatrix}
\]

To us, \(f_{\Phi \Sigma}\) is the most important frequency channel since it is both \(\Phi\)-odd and \(\Sigma\)-odd, thus isolating the PV component of the two vibrational transitions of \(L\) and \(R\). The other channels are used to tune the experiment and to probe sources of systematic error. For example, the \(f_\Sigma\) channel can be used to measure any \(\Sigma\)-odd effects between states \(|2\rangle\) and \(|3\rangle\) such as Zeeman shifts with different g-factors for the states. These can be corrected with a \(\delta_\Sigma\) offset.

When states \(|2\rangle\) and \(|3\rangle\) are measured simultaneously in a resolved manner, the two \(\Sigma\)-odd channels, \(f_\Sigma\) and \(f_{\Phi \Sigma}\), benefit from common mode noise suppression. This includes dissociation laser noise, which can be classified as proportional number noise, and magnetic field noise, which manifests as frequency noise. Number noise effects cancel to first order when taking the difference of \(N_{\tilde{\Phi},\Sigma^+} - N_{\tilde{\Phi},\Sigma^-}\). Importantly, frequency noise effects are also suppressed for such a term when \(N_{\tilde{\Phi},\Sigma^+} + N_{\tilde{\Phi},\Sigma^-}\) are in-phase. Similar noise rejection has been demonstrated to achieve the SQL in a noisy photo-dissociation measurement of the permanent electric dipole moment of the electron [33]. The two states can also be read out sequentially by any state-selective technique such as fluorescence, state-selective photo-ionization/photo-dissociation, or state dependent chemistry if simultaneous measurement is not possible. This slightly reduces the number of suppressed noise sources.

In order to test our sensitivity to changes in the experiment parameters, we varied the relative areas of each of the pulses in the sequence. We define the contrast of the fringe in state \(\tilde{\Sigma}\) as

\[
C_{\Sigma} = \left| N^{(L)}_{\Sigma} - N^{(R)}_{\Sigma} \right| / \bar{N}
\]

where \(N^{(k)}_{\Sigma}\) is the amplitude of the population oscillation of the enantiomer \(\tilde{\kappa}\) in state \(\tilde{\Sigma}\). We also define the leakage for the specific case of \(\tilde{\Phi} = -1\) as

\[
\text{Leakage} = \left( N^{(R)}_{|2\rangle} + N^{(L)}_{|3\rangle} \right) / 2
\]
Free evolution time [s]

\[
\Delta_{\text{PV}} = \frac{N_{2}^{(L)} + N_{3}^{(R)}}{N_{0}^{(L)} + N_{0}^{(R)}}
\]

which describes the average amplitude of the contaminant enantiomer that is not expected in each state for perfect pulses. For the case of \( \Phi = 1 \) the leakage definition is \( (N_{2}^{(L)} + N_{3}^{(R)})/2 \). The contrast and leakage are plotted in Fig. 4a, b) for a variation of each pulse area. When these variations are stabilized to within 10\%, the contrast is more than 0.88 and the leakage is less than 0.01.

Fig. 4c) shows a case with substantial leakage in the fringes due to a large 50\% error in the area of pulse S3. The spectrum observed in states \( |2\rangle \) and \( |3\rangle \) shows the opposite enantiomer frequency as a small feature on the sides of the main peaks [Fig. 4(d)]. This leakage may seem to be a detrimental systematic in the scheme, but would only lead to an underestimation of \( \Delta_{\text{PV}}^{\text{vib}} \).

Fortunately, adequately narrow lasers for coherent excitation in this range have already been demonstrated [24]. Alternatively, an Optical Parametric Oscillator (OPO) laser can be used [35]. Connecting pure rotational transitions such as states \( |2\rangle \) and \( |3\rangle \) is ubiquitous in three-wave mixing schemes.

The scheme phases, wavelengths, and Rabi rates can be optimized experimentally despite the use of a racemic sample by using 2 sequential stages of three-wave mixing with a total of 5 states. The sign of \( \Delta_{\text{PV}}^{\text{vib}} \) can be measured using a small sample with enantiomeric excess. This is a less stringent requirement than using such a sample for the entire experiment. Alternatively, concatenation of other methods to our scheme, such as Coulomb explosion [10], can be used to determine the absolute configuration of the molecules [30]. To our knowledge, measuring \( \Delta_{\phi} \) for the fields and comparing the sign of the transition dipole moment components is not reliable in extracting the molecule’s absolute configuration [30].

We have presented a framework to perform PV precision measurement in a racemic sample of chiral molecules that is readily applicable to existing experiments using vibrational spectroscopy [25] as well as pure rotational three-wave mixing [24] [36]. The differential scheme benefits from common-mode noise rejection such that statistical uncertainty estimations at the SQL are realistic. Our own plan is to realize this method with charged chiral molecules, which can be trapped, facilitating measurements at long coherence times [35]. Ionized versions of chiral molecules have also been suggested to substantially enhance PV [12]. Our upcoming work discusses several chiral molecular ion candidates for PV measurement [11].

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Fig. 4. Sensitivity of the contrast (a) and enantiomer leakage (b) due to an inaccurate area of each pulse. Additionally, P/Q denotes variation of the ratio between the areas of the P and Q pulses. (c) A Ramsey sequence, showing significant oscillation contamination of the wrong enantiomer (leakage) for \( \Phi = -1 \), is created with a variation of 50\% in S3 [green squares in (a,b)]. This contamination can be observed in the spectra of the total populations (d), but would only lead to an underestimation of \( \Delta_{\text{PV}}^{\text{vib}} \).

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