

Influence of Parity Violating Weak Nuclear Potentials on Vibrational and Rotational Frequencies in Chiral Molecules

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We study the effect of parity violation on the vibrational and rotational frequencies of CHBrClF. We report the parity violating potentials as a function of reduced normal coordinates for all nine internal vibrational modes ω_1 to ω_9 , using our new, accurate multiconfigurational-linear response (RPA and complete-active-space self-consistent field) approach. All modes ω_i show a strongly mode dependent relative shift $\Delta_{\text{pv}}\omega_i/\omega_i$ (between 0.08×10^{-16} and 13.3×10^{-16} , much smaller than all previous experimental tests could detect, including the most recent ones). The results are discussed in relation to other tests of parity violation.

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1. Introduction.—Relatively quickly after the discovery of parity violation in atomic and nuclear physics [1,2] it was recognized that this phenomenon can lead to an energy difference $\Delta_{\text{pv}}E$ between left-handed and right-handed enantiomers of chiral molecules ([3–8]; for a review, see [9]). While direct measurements of $\Delta_{\text{pv}}E$ have been proposed, using spectroscopic methods involving intermediate levels of well-defined parity [9,10], until today no successful experiment of this or a related kind has been reported. There have, however, been substantial efforts to calculate $\Delta_{\text{pv}}E$ quantitatively, following the pioneering work of Hegstrom, Rein, and Sandars about two decades ago [11–14]. Such calculations are possible because of electroweak theory [15–17] providing a general theoretical framework for parity violating effects not only in high energy and nuclear physics, but also in atomic [18,19] and molecular physics, where we have termed the systematic approach to parity violation “electroweak quantum chemistry” [20–23]. The recent theoretical discovery [20,21], reconfirmed by independent computational techniques [22–25], that $\Delta_{\text{pv}}E$ for several molecular examples is calculated by configuration interaction singles and other more advanced theoretical methods to be larger by 1 to 2 orders of magnitude than anticipated by the earlier restricted Hartree-Fock (RHF) methods has led to a renewed interest in parity violating effects in molecules.

Among the proposals to establish parity violation in molecules, one may mention also the possibility of measuring frequency shifts $\Delta_{\text{pv}}\nu$ in spectra of enantiomers, ranging from the radio frequency (NMR) [26,27] to the infrared [5,28–36]. Indeed some early theoretical estimates of these effects are available [13]. In this context [5,28], as well as in the context of direct measurements of $\Delta_{\text{pv}}E$ [9], CHBrClF has been selected as a test compound and recently been investigated in more detail [31–36]. Together with fluorooxirane [30], CHBrClF has been the first example of a chiral molecule, for which an infrared fundamental was fully rotationally analyzed using a combination of advanced Fourier transform infrared (FTIR) and diode

laser supersonic jet techniques along with microwave experiments. This provides a prerequisite of experimental tests of parity violation in the optical domain [34]. Such experiments provide bounds on $\Delta_{\text{pv}}\nu/\nu$, since splittings from the different enantiomers are not resolved with an accuracy limited by jet Doppler widths in microwave and IR spectra (in the range of 10^{-6} to 10^{-7}). This upper limit has already been discussed earlier [5,28,29], including experiments with sub-Doppler resolution. Recently, Daussy *et al.* have provided a much more stringent result in the infrared spectrum of CHBrClF, i.e., $\Delta_{\text{pv}}\nu/\nu < 4 \times 10^{-13}$ [35,36]. While bounds on the shift do not provide a direct measurement of the actual parity violating energy difference $\Delta_{\text{pv}}E$ between the enantiomers, they are nevertheless of interest in comparison with theory. So far, accurate theoretical calculations on $\Delta_{\text{pv}}\nu$ in CHBrClF (nor any other chiral molecule, to our knowledge) have not yet been reported. It is the aim of this paper to provide such results on the basis of our systematic approaches towards electroweak quantum chemistry [20–23].

2. Theory.—One can distinguish two fundamentally different approaches towards calculating $\Delta_{\text{pv}}\nu$ in rovibrational spectra of chiral molecules. The first one might be called “adiabatic,” because it makes proper use of the large difference in frequency and time scales resulting from rovibronic and parity violating energies. One calculates the rovibronic wave functions and energy levels E_i (in $3N - 3$ dimensional space, $3N - 6$ with separation of rotation and vibration) and then the shifts $\delta_{\text{pv}}E_i^l$ and $\delta_{\text{pv}}E_i^r$ for the energy levels of left- and right-handed enantiomers by perturbation theory, using the parity violating Hamiltonian. By calculating $(\delta_{\text{pv}}E_i^l - \delta_{\text{pv}}E_j^l) - (\delta_{\text{pv}}E_i^r - \delta_{\text{pv}}E_j^r) = h\Delta_{\text{pv}}\nu_{ij}$ one obtains the desired results for measurable shifts of transition frequencies. While this approach would be theoretically most satisfactory, it demands coping with the formidable task of calculating the full dimensional rovibronic wave function for a molecule like CHBrClF. Even if a separation of electronic, vibrational, and rotational degrees of freedom is accepted as an

approximation, just the solution of the nonseparable anharmonic nine-dimensional vibrational problem is a task, which has only recently been accomplished for systems of related complexity in exact discussions of rovibrational constants and dipole moments of methane isotopomers, using quantum Monte Carlo techniques [37]. This approach does not seem attractive for a first study of $\Delta_{\text{pv}}\nu$, although it should be kept in mind for the future. If one introduced further separability approximations, one expects errors of the size estimated for the other approach selected here.

The second approach might be called “quasiharmonic reverse adiabatic.” In order to estimate the influence of the parity violating potential on the vibrational and rotational frequencies, we calculate the function $V_{\text{pv}}(\vec{q})$ in reduced dimensionless normal coordinates q_j (j from 1 to $3N - 6$). \vec{q} corresponds to a set of $3N$ Cartesian coordinates for a N -atomic molecule. Following our earlier work on multidimensional potential energy surfaces for the CH chromophore [31,38–40], we obtain reduced normal coordinates q_j from the diagonalization of the Cartesian mass-weighted force constant matrix $\mathbf{F}^{(x,m)}$. We determine $V_{\text{pv}}(\vec{q})$ along the reduced normal coordinates via the Cartesian displacements [41]

$$\Delta x_n^{(j)} = m_n^{-1/2} l_{nj} \gamma_j^{-1/2} \Delta q_j, \quad (1)$$

where $\gamma_j = \sqrt{\omega_j^0/\hbar}$ and $\{\omega_j^0\}$ are related to the eigenvalues, and $\{l_{nj}\}$ are the eigenvectors obtained by diagonalizing $\mathbf{F}^{(x,m)}$; m_n are the atomic masses and x_n the atomic Cartesian coordinates. This provides new Cartesian geometries used to calculate $V_{\text{pv}}(q_j)$.

To a first approximation we assume that $V_{\text{pv}}(\vec{q})$ is diagonal, without coupling between different vibrational modes. An estimate for the anharmonic vibrational fundamental wave number shift between enantiomers, $\Delta_{\text{pv}}\tilde{\nu}_j$ can be obtained by assuming that it is approximately equal to the shift of the harmonic wave numbers (the factor of 2 arises since we consider the difference between both enantiomers):

$$\Delta_{\text{pv}}\tilde{\nu}_j \approx \Delta_{\text{pv}}\tilde{\omega}_j(\tilde{\nu}_j/\tilde{\omega}_j) \approx \frac{2}{hc} [\mathbf{l}_0^\dagger \mathbf{F}_{\text{pv}} \mathbf{l}_0]_{jj} (\tilde{\nu}_j/\tilde{\omega}_j). \quad (2)$$

\mathbf{l}_0 diagonalizes $\mathbf{F}^{(x,m)}$, and the perturbing force constant matrix due to the parity violating potential, \mathbf{F}_{pv} , is evaluated as the second derivative of $V_{\text{pv}}(\vec{q})$ with respect to the $3N - 6$ reduced normal coordinates. The diagonal force constants are given by

$$\frac{F_{\text{pv}}(j)}{hc} = \frac{1}{hc} \left(\frac{\partial^2 V_{\text{pv}}(\vec{q})}{\partial q_j^2} \right)_{q_i \neq j} = 2p_2(j). \quad (3)$$

$V_{\text{pv}}(\vec{q})$ has been calculated *ab initio* on a grid and fitted by a least-squares procedure to a polynomial expansion [Eq. (4)] up to a third order, with coefficients $p_k(j)$:

$$\begin{aligned} \frac{V(q_j)}{hc} &= \frac{1}{2} \tilde{\omega}_j^0 q_j^2 + \frac{V_{\text{pv}}(q_j)}{hc} \\ &= \frac{1}{2} \tilde{\omega}_j^0 q_j^2 + \sum_{k=0}^3 p_k(j) q_j^k. \end{aligned} \quad (4)$$

Thus, we have for both (R) and (S) enantiomers $\tilde{\omega}_j \approx \tilde{\omega}_j^0 + 2p_2(j)$:

$$\tilde{\omega}_j^R - \tilde{\omega}_j^S \approx 4p_2^R(j) \approx \Delta_{\text{pv}}\tilde{\omega}_j, \quad (5)$$

where $p_2^R \approx -p_2^S$, which has been checked numerically. CHBrCIF has been investigated theoretically and spectroscopically by high-resolution diode laser and FTIR vibrational overtone spectroscopy of the CH chromophore [31–33]. The vibrational force field has been obtained at the level of second order Møller-Plesset perturbation theory (MP2) with basis 1 (double-zeta quality) from our previous investigations [32]. We evaluated $V_{\text{pv}}(q_j)$ for wave functions from RHF theory in the sum-over-states approach [20,21], and with our most recent multiconfigurational-linear response (MC-LR) approach [23] using the RPA and complete-active-space self-consistent field (CASSCF), the latter only for some selected vibrational modes. The relevant quadratic parameters $p_2(j)$ from the least-squares fit have been used to calculate $\Delta_{\text{pv}}\tilde{\omega}_j/\tilde{\omega}_j$, listed in Table I, for the nine vibrational modes as obtained from RHF and RPA.

V_{pv} also gives rise to a shift of the global potential minimum. This change in equilibrium geometry parallels a change of the effective rotational constants and thus can be used to estimate the frequency shifts in the pure rotational spectrum in the microwave region: For each vibrational mode (uncoupled, but due to V_{pv} no longer harmonic), we have a coordinate dependence (expressed in reduced normal coordinates of the molecular system without V_{pv} present) according to Eq. (4), and the coordinate for the new minimum is approximately given by the expression (assuming $q_{j \text{ min}} = 0$ without V_{pv})

$$q_{j \text{ min}} \approx -p_1(j)/\tilde{\omega}_j^0. \quad (6)$$

The corresponding change in geometry ($\Delta\vec{x}$) is given by Eq. (1). This change in Cartesian geometry gives rise to a slightly modified inertia tensor $\mathbf{I}^0 + \mathbf{I}_{\text{pv}}$ compared to \mathbf{I}^0 without V_{pv} present. The eigenvalues of $\mathbf{Z}^\dagger(\mathbf{I}^0 + \mathbf{I}_{\text{pv}})\mathbf{Z}$ (\mathbf{Z} is the matrix of eigenvectors) provide an estimate for

TABLE I. Harmonic vibrational wave numbers $\tilde{\omega}$ (in cm^{-1}) and shifts $\Delta\tilde{\omega}_j/\tilde{\omega}_j$ for (R)- $\text{CH}^{79}\text{Bi}^{35}\text{CIF}$. The second column gives experimental, anharmonic fundamental wave numbers. The third column provides harmonic wave numbers from Refs. [31,32] obtained with a basis set of essentially double-zeta quality. RPA and RHF relative shifts have been obtained with a valence double-zeta basis set [42].

j	$\tilde{\nu}_j^{\text{exp}}/\text{cm}^{-1}$ [32]	$\tilde{\omega}_j/\text{cm}^{-1}$	$\frac{\Delta_{\text{pv}}\tilde{\omega}_j}{\tilde{\omega}_j}/10^{-19}$	
			RHF	RPA
1	3025.5	3245.000	-13.9	-83.2
2	1306.2	1375.227	+1134.0	+3341.4
3	1202.8	1315.363	-1173.3	-3003.1
4	1077.2	1097.851	+348.9	+611.8
5	787.0	838.309	-1613.6	-2999.2
6	663.6	680.406	+385.4	+1186.8
7	425.2	437.436	-498.5	+721.4
8	313.0	327.435	+490.9	-587.7
9	223.6	240.356	-150.5	-385.2

the change in the principal moments of inertia I^{PP} due to the parity violating potential. The magnitude of the difference between the enantiomers $\Delta_{pv}A = A^R - A^S$ is twice the magnitude of this change. Again, a more accurate calculation of $\Delta_{pv}A$ would use the expectation value taken over rotational levels of the vibrational ground state [37].

3. Results and discussion.—The dependence of the parity violating potential $V_{pv}(q_j)$ of (*R*)-CHBrCIF on reduced normal coordinates is presented in Fig. 1 for two selected vibrational degrees of freedom, the CF-stretching mode ν_4 at 1077 cm^{-1} and the higher CH-bending mode ν_2 at 1306 cm^{-1} . We show the one-dimensional functions $V_{pv}(q_j)$ in the reduced normal coordinate range $-2 \leq q_j \leq +2$ [this can be converted to a normal coordinate range for Q_j with $Q_j/(\text{\AA}\sqrt{u}) \approx q_j \times \sqrt{33.71527/(\tilde{\omega}_j/\text{cm}^{-1})}$].

The variation of V_{pv} with q_j is qualitatively similar for the RHF and the RPA calculations, however, there are quantitative differences (up to a factor of 6; see Table I and Fig. 1). There are also great differences between the vibrational modes. The parity violating potential energy is almost constant over the whole q range for the CH-stretching vibration ν_1 . The bending modes ν_2, ν_3 (CH bend), ν_7 (CICF bend), and ν_8 (BrCF bend) have comparably large V_{pv} values for large q_j (see Fig. 1 for the examples ν_2 and ν_4). We have explicitly calculated V_{pv} for the (*S*)-CHBrCIF enantiomer. The fit gives, within numerical accuracy, the same magnitude but different signs, as expected. The largest relative shift in the harmonic vibrational frequencies due to the parity violating potential is obtained for the CH-bending (ν_2, ν_3) and the CCl-stretching (ν_5) vibrations (with both RHF and RPA).

The relative difference $\Delta_{pv}X/X$ of the *A, B, C* rotational constants between both enantiomers caused by V_{pv} is on the order of 10^{-16} (between 0.1 and 0.3), whereas the current relative experimental accuracy of the *A* constant is about 10^{-8} . Given that rotational transition wave

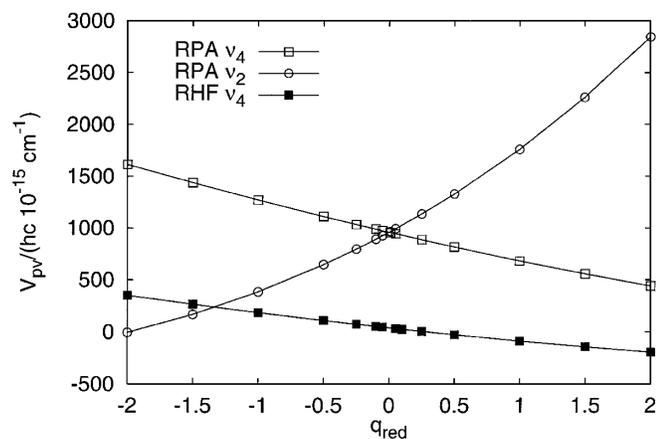


FIG. 1. V_{pv} as a function of the dimensionless reduced normal coordinate for the (*R*)-CHBrCIF enantiomer: ν_4 (open squares), ν_2 (open circles) as obtained from RPA, and ν_4 (filled squares) from RHF.

numbers are on the order of $2BJ$ with the angular momentum quantum number J , detection of shifts due to parity violation might be easier in the microwave rather than in the IR spectra.

Finally, Table II shows the parameters from the fit of V_{pv} for the CF-stretching mode (ν_4) to the third order polynomial Eq. (4) for RHF, RPA, and three high quality MC-LR (CASSCF) wave functions by steadily increasing the active space from 8 electrons distributed over 10 orbitals ([8,10] CAS) to finally 12 electrons in 12 orbitals (already a fairly large active space). The energy difference between (*S*)- and (*R*)-CHBrCIF, $\Delta_{pv}E = E^R - E^S$ can be calculated from the averaged value $(2hc/9)\sum_j p_0(j) \approx 2hcp_0(j)^R$, and the wave number shift is $\Delta_{pv}\tilde{\omega}_j \approx 4p_2(j)$.

4. Conclusions.—The present work provides the first reasonably accurate theoretical calculations on frequency shifts in the infrared and microwave spectra of the enantiomers of chiral molecules due to the effects of the parity violating weak nuclear interaction. The application to CHBrCIF indicates that currently available experimental tests in the ν_4 infrared spectrum (with uncertainty 4×10^{-13}) miss the predicted effect ($\Delta_{pv}\omega/\omega \approx 6 \times 10^{-17}$) by about 4 orders of magnitude. The predicted shifts depend strongly on the vibrational mode. The predicted relative effect in the microwave spectrum (2×10^{-17} for $\Delta_{pv}C/C$) is also far from the current experimental uncertainty ($\Delta C/C \approx 2 \times 10^{-7}$). The *S* configuration of CHBrCIF is calculated here to be more stable than *R* by about 10^{-12} cm^{-1} or about $10^{-11}\text{ J mol}^{-1}$ (for the absolute configuration, see [43]).

In assessing the significance of our results three considerations are in order. First, larger experimental effects are expected for chiral molecules with at least *two heavy* centers [21], such as CHBrFI, where the shift might be detectable in the near future. While relativistic effects [25] will be of some importance for all of these molecules, they are not expected to change the order of magnitude for CHBrCIF (a relativistic result reported for $\Delta_{pv}E$ in CHBrCIF is obviously grossly incorrect [44]). Second, theoretical improvements are desirable as discussed at the beginning of section 2. A first such step has been carried out by calculating expectation values $\langle \nu | V_{pv} | \nu \rangle$ for one-dimensional harmonic and anharmonic vibrational levels

TABLE II. Most important polynomial fit coefficients p_i in 10^{-15} cm^{-1} for ν_4 of (*R*)-CHBrCIF obtained with different *ab initio* methods, namely, RHF, RPA, and MC-LR (CASSCF). The standard deviation of the least-squares fit is given in parentheses in units of the last significant digit.

Method	p_0	p_1	p_2
RHF	38.87(1)	-135.76(1)	9.57(0)
RPA	958.80(3)	-294.06(6)	16.79(2)
[8,10] CAS	799.21(3)	-258.52(6)	18.66(2)
[8,12] CAS	783.63(8)	-265.08(2)	19.47(4)
[12,12] CAS	962.70(5)	-246.65(9)	14.71(3)

(in reduced normal coordinates), giving results lower by a factor of 2 than those presented here in the harmonic case and variable changes in absolute magnitude of this order for the anharmonic case. The difference is understandable and gives an indication of the uncertainties due to the approximations in the theory [45]. Third, a direct measurement of the much larger predicted $\Delta_{pv}E$ using an intermediate spectroscopic level connecting both enantiomers as proposed in [9,10] would, because of its higher significance, be more useful in theoretically analyzing the experimental result with the aim of improving our knowledge of the fundamental constants of the standard model [20–22] (see also the discussion in atomic parity violation [18,19,46]) and other aspects of fundamental symmetries [40,47].

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