Parity-Violation Effects in the C-F Stretching Mode of Heavy-Atom Methyl Fluorides

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Relativistic four-component electronic structure calculations including parity-odd electroweak interactions give unprecedented large energy differences of 158 mHz for $PH_3AuCHFCl$ and 219 mHz for ClHgCHFCl for the C-F stretching mode of the corresponding enantiomeric compounds. This signifies a considerable improvement over previous predictions for chiral methyl compounds of the form $CHXYZ$ ($X, Y, Z =$ F, Cl, Br, or I). These organometallic compounds are therefore ideal for future high resolution spectroscopy experiments.

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Although it is well accepted that parity violation (PV) effects lift the degeneracy between mirror image molecules (enantiomers) of chiral compounds [1,2], such small effects have not been unambiguously identified yet [3,4] despite a number of more recent positive claims [5]. The search for the breakdown of mirror image symmetry in chiral compounds therefore remains an unresolved problem in molecular physics [6].

Any success in finding P-odd effects in molecules relies on improving the ratio $\Delta\nu_{RS}^{\mathrm{PV}}/\nu_R^{\mathrm{PV}}$, where $\Delta\nu_{RS}^{\mathrm{PV}} = \nu_R^{\mathrm{PV}} - \nu_S^{\mathrm{PV}}$ and ν_R^{PV} describes the transition (electronic, vibrational, etc.) including PV effects for the right-handed molecule (according to the Cahn-Ingold-Prelog definition). Current high resolution experiments using tunable CO_2 lasers reach $\Delta\nu = \sim 1$ Hz [4,7], but recent developments in enhancing the resolution could lead to further improvements down to the 10 mHz range [8,9]. Since CO_2 lasers are tunable between 800–1200 cm^{-1}, current experiments focus almost exclusively on C-F stretching modes in chiral methane derivates. Furthermore, PV effects scale with the nuclear charge approximately like Z^5 [10]. Heavy atoms are therefore attached to the carbon center which according to the single-center theorem by Hegstrom [11] should increase the PV energy difference between the enantiomers. Coupling of the C-F stretching mode with other modes involving the heavier atoms should subsequently improve $\Delta\nu_{RS}^{\mathrm{PV}}/\nu_R^{\mathrm{PV}}$.

It is a nontrivial issue to find suitable chiral compounds including heavier elements which are both thermodynamically stable and have vibrational modes in the right frequency range. The thermodynamic stability of high oxidation state isoelectronic compounds usually decreases with increasing atomic number, e.g., the molecule PbHFClBr [10] is not considered an ideal candidate because it would decompose easily. Previous theoretical work therefore focused on the thermodynamically stable methane derivates [12–15] which gave $\Delta\nu_{RS} = 1.7$, 12, 24, and 51 mHz for CHFClBr, CFClBrI, CHFClI, and CHFBrI, respectively [12]. The results suggest that, while the PV energy difference between enantiomers is quite sensitive on the theoretical model applied, the vibrational corrections which depend on the first and second derivative of the PV energy shift with respect to the normal coordinate agree between the different models if anharmonic corrections are considered. If heavy atoms are involved, the most rigorous way to account for PV effects is through the use of a four-component relativistic scheme using the Dirac-Coulomb Hamiltonian and the PV operator in its relativistic (and most convenient) form.

Here we report PV calculations on the molecules $PH_3AuCHFCl$ and ClHgCHFCl to improve the current limit on the $\Delta\nu_{RS}^{\mathrm{PV}}/\nu_R^{\mathrm{PV}}$ ratio. These compounds were found from an intensive literature search of thermodynamically stable organometallic compounds. Nonchiral derivates of both compounds are known [16,17]. We carried out scalar relativistic Hartree-Fock calculations using second-order many-body (MBPT2) theory to account for electron correlation [18]. Small core relativistic pseudopotentials of the Stuttgart group [19] were used together with large sized valence basis sets for Au and Hg, and aug-cc-pVDZ all-electron basis sets of Dunning *et al.* [20–22] for all the other atoms. Geometry optimizations and subsequent frequency analyses gave the infrared spectra shown in Fig. 1 which are useful for the future identification of these compounds. A normal mode analysis at the MBPT2 level gave the harmonic force field F_{ij} and displacement coordinates Δx_i for the C-F stretching mode, which is the most intensive ir mode (Fig. 1). Along the C-F normal coordinate, the MBPT2 potential energy curve $V(x)$ was calculated stepwise and fitted to a polynomial of sufficiently high order. The potential energy curves for both compounds are shown in Fig. 2.

Relativistic Hartree-Fock calculations were performed employing the Dirac-Coulomb Hamiltonian within the program package DIRAC [23]. The basis sets for H, C, F, and Cl were uncontracted cc-pVDZ + np sets as detailed previously [13]. For Au and Hg, the dual-type all-electron sets of Dyall were used [24]. The dominant part of the parity violating contribution is expressed by the (nuclear spin independent) P-odd operator

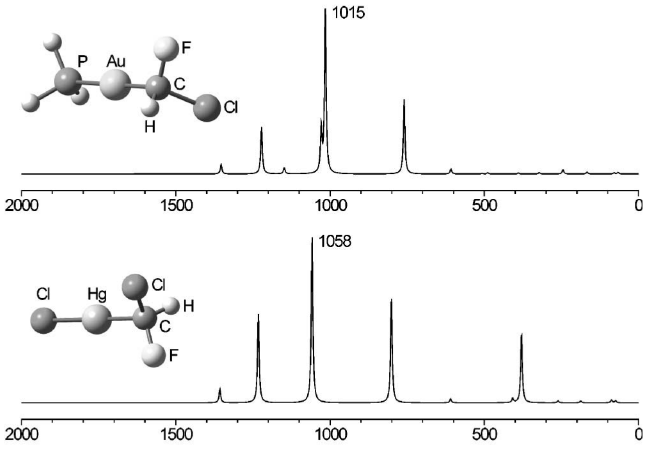

FIG. 1. Simulated infrared spectrum for $PH_3AuCHFCl$ and ClHgCHFCl (in cm^{-1}) using Lorentzian line shapes. The optimized structures of both species in the R configuration are also shown.

$$H_p = \frac{G_F}{2\sqrt{2}} \sum_{i,n} Q_{W,n} \gamma_i^5 \varrho_n(r_i), \tag{1}$$

where $G_F = 2.222\,55 \times 10^{-14}$ a.u. is the Fermi coupling constant and γ^5 the pseudoscalar chirality operator. The summation is over electrons, i, and nuclei, n, and the energy difference between the left- and right-handed forms of the molecule is $\Delta E_{\mathrm{PV}} = 2E_{\mathrm{PV}}$. ϱ_n is the nuclear charge distribution [25] and a Gaussian charge distribution as described in Ref. [26] was chosen. The weak charge of nucleus n is $Q_{W,n} = -N_n + Z_n(1 - 4\sin^2\theta_W)$, where N_n and Z_n are the numbers of neutrons and protons, respectively. A value of $\sin^2\theta_W = 0.2319$ was chosen for the Weinberg mixing angle. For the isotopes $A_n = N_n + Z_n$, values of 1, 12, 19, 35, 197, and 202 for H, C, F, Cl, Au, and Hg were used, respectively. The parity violating energy shift E_{PV} at a given geometry along the normal coordinate of the C-F stretching mode was obtained from perturbation theory at the Dirac-Hartree-Fock level:

$$E_{\mathrm{PV}} = \langle \Psi_{\mathrm{DHF}} | H_p | \Psi_{\mathrm{DHF}} \rangle. \tag{2}$$

The parity violating matrix elements $E_{\mathrm{PV}}(x)$ were calculated pointwise along the MBPT2 potential energy curve $V(x)$ and fitted to a polynomial (Fig. 2). The molecules were chosen in the R configuration as shown in Fig. 1 which determines the sign of E_{PV}. A numerical frequency analysis using the Numerov-Cooley procedure gave the PV energy shifts for each vibrational level with quantum number n. Note that this analysis neglects higher order coupling with other modes and electron correlation effects in Eq. (2), but will nevertheless be indicative of the PV energy shifts expected for the C-F stretching mode.

At the equilibrium geometry, we obtain $E_{\mathrm{PV}} = 4.15$ and 4.25 Hz for $PH_3AuCHFCl$ and ClHgCHFCl, respectively (here we use 1 a.u. $= 6.579\,683\,74 \times 10^{15}$ Hz for conversion of energy units). This is well below the largest PV energy shifts obtained thus far for a number of heavy metal compounds, e.g., 158 Hz for $(C_5H_5)Re(CO)(NO)I$ [27] or 47 Hz for BiHFBr [28]. However, these compounds are less useful for high resolution vibrational spectroscopy. The solution of the vibrational Schrödinger equation gave the $n = 0 \rightarrow m$ transitions listed in Table I up to $m = 5$. The parity violation energy difference for the C-F mode fundamental transition between both enantiomers is therefore $\Delta E_{\mathrm{PV}} = 158$ mHz for $PH_3AuCHFCl$ and 219 mHz for ClHgCHFCl. This is a factor 3 to 4 improvement in magnitude over the previously calculated PV frequency shifts for CHFBrI.

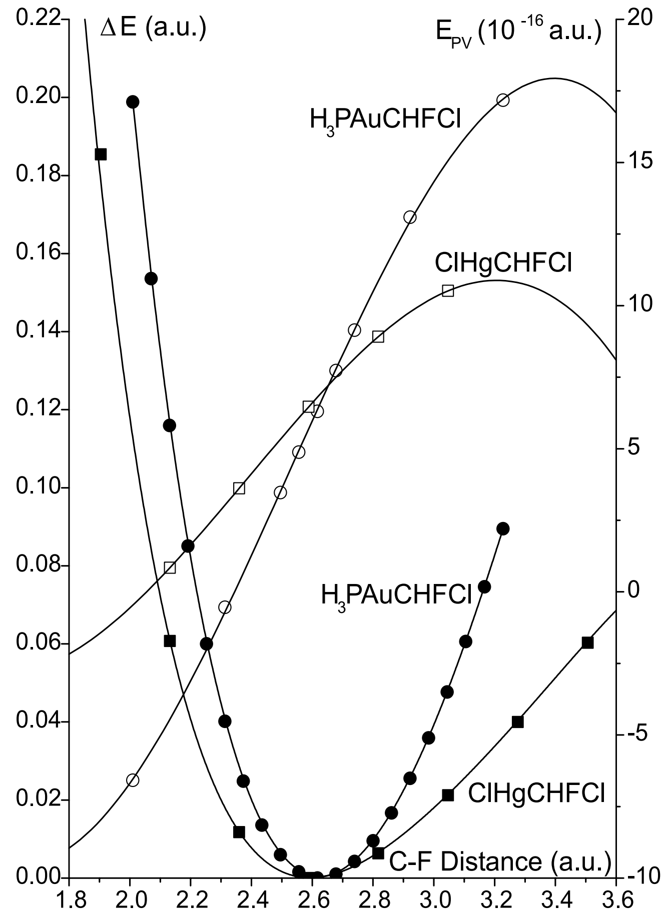

FIG. 2. Potential energy curves (left axis, filled symbols) and parity violation energy shift (right axis, open symbols) for $PH_3AuCHFCl$ and ClHgCHFCl (in a.u.).

TABLE I. PV contributions to vibrational transitions ($n = 0 \rightarrow m$) for the C-F stretching mode (in mHz) in the R configuration.

0 →	1	2	3	4	5
$PH_3AuCHFCl$	79.0	156.3	231.8	305.7	377.8
ClHgCHFCl	109.6	209.5	299.1	377.7	444.8

We note $\Delta\nu_{RS}^{\mathrm{PV}}/\nu_R^{\mathrm{PV}} = 5.2 \times 10^{-15}$ for the gold and 6.9×10^{-15} for the mercury compound. These ratios are considerably better than the originally estimated values of 10^{-16}–10^{-17} by Letokhov [2] for vibrational PV effects, although far away from more optimistic predictions made by Zel'dovich *et al.* [29]. For the $h\nu_R^{\mathrm{PV}}/E_{\mathrm{PV}}$ ratio, we obtain smaller values (0.019 and 0.026) compared to the chiral methane species studied before (0.05–0.09) [12]. This implies weaker coupling with vibrational modes involving the heavy elements Au and Hg. It also suggests that it will be very difficult to achieve much higher values for PV effects in C-F stretching modes. We note that at certain geometries the PV energy shift is zero (Fig. 2), a well-known fact found for other chiral molecules as well [30]. From this it follows that chirality does not necessarily imply a nonzero PV contribution.

As mentioned above, derivates of both compounds studied here are known and characterized, i.e., $P(CH_3)_3AuCF_3$ and $ClHgCHCl_2$ are both stable compounds at room temperature [16,17]. We suggest the synthesis of the corresponding chiral species to obtain the enantiomers in pure form. High resolution spectroscopy using CO_2 lasers may reveal parity violation effects in chiral molecules for the first time.

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