

Large Parity Violation Effects in the Vibrational Spectrum of Organometallic Compounds

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The understanding of chirality is central to molecular sciences. Barron defines chirality as exhibited by systems that exist in two distinct enantiomeric states that are interconverted by the parity operation (space inversion), but not by time reversal combined with any proper spatial rotation.¹ Conservation of parity symmetry² manifests itself in enantiomers having exactly the same chemical and physical properties (in an achiral medium). According to the standard model,^{3–5} the neutral weak electron–nucleon current leads to parity violation (breakdown of mirror image symmetry or parity nonconservation, PNC) in chiral molecules, thus causing a small energy difference ΔE_{PNC} between enantiomers resulting in small differences in spectroscopic properties.^{6–9}

PNC effects, albeit very small, have been observed in electronic transitions of heavy atoms^{10,11} and so far confirm the standard model.¹² For known chiral compounds, such effects are predicted to be in the millihertz range,^{13–15} and at least 1 or 2 orders below the current experimental detection limit.¹⁶ Consequently, all spectroscopic attempts, by either vibrational, NMR, or Mössbauer spectroscopy, to detect such parity violation energy differences in chiral molecules have failed so far.^{17–20} Thermodynamically stable molecules with a heavy element at the chiral center suitable for the detection of vibrational PNC effects have not been found yet. Here, we predict from ab initio relativistic calculations large parity violation energy differences of about 1 Hz for vibrational transitions in organometallic compounds, which now should become accessible to high-resolution optical spectroscopy experiments carried out in the CO₂ laser frequency range.

PNC effects in molecules scale like Z^n (approximately $n = 3$ for the nuclear spin-dependent PNC part,²¹ and $n = 5$ for the nuclear spin-independent part²²),¹¹ which implies that heavy elements are ideal for detecting PNC in chiral molecules. It is currently a nontrivial issue to identify chiral compounds including heavy elements suitable for high-resolution experiments. Mössbauer or NMR spectroscopy faces the difficulty that it has to be carried out in the solid state or solution, thus introducing environmental effects difficult to control. Perhaps the most promising way to detect molecular PNC is by high-resolution vibrational spectroscopy using a tunable CO₂ laser in the 878–1108 cm⁻¹ range.¹⁹ This immediately imposes another major difficulty in finding a heavy element system with stretching or bending frequencies in this particular frequency range. Attaching heavy metals to light atom centers enhances PNC effects, but currently limits such effects to about 200 mHz for the C–F stretching mode in Cl–Hg–CHFCl, for example.¹⁵ The only other proposed compound is BiHFX (X = Br, I), where a few hertz of PNC is obtained for the H–Bi–X bending mode at 400–500 cm⁻¹.²³ However, this compound is most likely thermodynamically unstable and would involve the observation of PNC in vibrational overtones.

Large PNC energy differences between enantiomers were recently reported for organometallic compounds including a heavy

metal atom center M.²⁴ To reach the CO₂ laser frequency range for metal–ligand M–L stretching frequencies, the M–L stretching force constant has to be reasonably large to counterbalance the large reduced mass between M and L. Therefore, thermodynamically stable chiral species are required with a light ligand to heavy metal double bond. After an extensive investigation, it appeared that the two most promising candidates in the literature are Os(η^5 -C₅H₅)(=CHPh)Cl(P^tPr₃) involving a Os=C double bond,²⁵ and Re(η^5 -Cp*)(=O)(CR₃)Cl (Cp* = C₅(CH₃)₅) involving a Re=O double bond.²⁶ For the osmium species, we replaced =CHPh as ligand by =CCl₂, as to introduce a large dipole moment along the Os=C axis, which enhances the intensity of the Os=C stretching mode. Both species are shown in Figure 1 together with their simulated infrared spectra important for the identification of these compounds and for a subsequent local mode analysis. The calculated harmonic frequencies for the Os=C and the Re=O stretching modes at $\nu_{\text{vib}} = 901$ and 989 cm⁻¹, respectively, are the most intense infrared transitions.

The structures of Os(η^5 -C₅H₅)(=CCl₂)Cl(PH₃) and Re(η^5 -Cp*)(=O)(CH₃)Cl were fully optimized using density functional theory (B3LYP) including scalar relativistic effects for the heavier elements by using Stuttgart small-core pseudopotentials.²⁷ Subsequent four-component all-electron Dirac–Fock calculations²⁸ gave the parity violation energy shift for a molecule with n nuclei and i electrons as an expectation value of the PNC operator, as implemented by our group, originating from the time-like ($V_n - A_e$) component of the weak neutral current between electrons and nucleons

$$E_{\text{PNC}} = \frac{G_{\text{F}}}{2\sqrt{2}} \langle \Psi | \sum_{n,i} Q_{\text{W},n} \gamma_i^5 \rho_n(\mathbf{r}_i) | \Psi \rangle$$

where $G_{\text{F}} = 2.22255 \times 10^{-14}$ au is the Fermi coupling constant, γ^5 is the 4×4 Dirac pseudoscalar chirality operator, and ρ is the average distribution of protons and neutrons within the nucleus. The weak charge $Q_{\text{W}} = -N + Z(1 - 4 \sin^2 \theta_{\text{W}})$ depends on the number of protons Z and neutrons N and the Weinberg mixing angle ($\sin^2 \theta_{\text{W}} = 0.2319$). For more computational details, see ref 24.

As expected, the total parity violation contribution to the electronic energy at the optimized geometry is quite large, $\Delta E_{\text{PNC}}(R-S) = 2E_{\text{PNC}}(R) = +6.29 \times 10^{-11}$ kJ mol⁻¹ (158 Hz) for the Os and $+2.17 \times 10^{-10}$ kJ mol⁻¹ (545 Hz) for the Re compound, with the by far largest PNC contribution coming directly from the chiral metal center (the sign given for E_{PNC} is that obtained for the R -configurations shown in Figure 1). This does not necessarily imply that the PNC energy differences in the vibrational transitions ($n \rightarrow n'$, n and n' are vibrational quantum numbers) are of a similar large magnitude. A local mode analysis along the metal–ligand stretching mode (Figure 2) gives PNC effects of $\nu_{\text{PNC}}(R; 0 \rightarrow 1) = -575$ mHz and $\nu_{\text{PNC}}(R; 0 \rightarrow 2) = -1147$ mHz for the Os=C stretching mode, and $\nu_{\text{PNC}}(R; 0 \rightarrow 1) = +546$ mHz and $\nu_{\text{PNC}}(R; 0 \rightarrow 2) = +1109$ mHz for the Re=O stretching mode. Hence, for the fundamental transition ($n = 0 \rightarrow 1$), we obtain $\Delta\nu_{\text{PNC}}(R-S) =$

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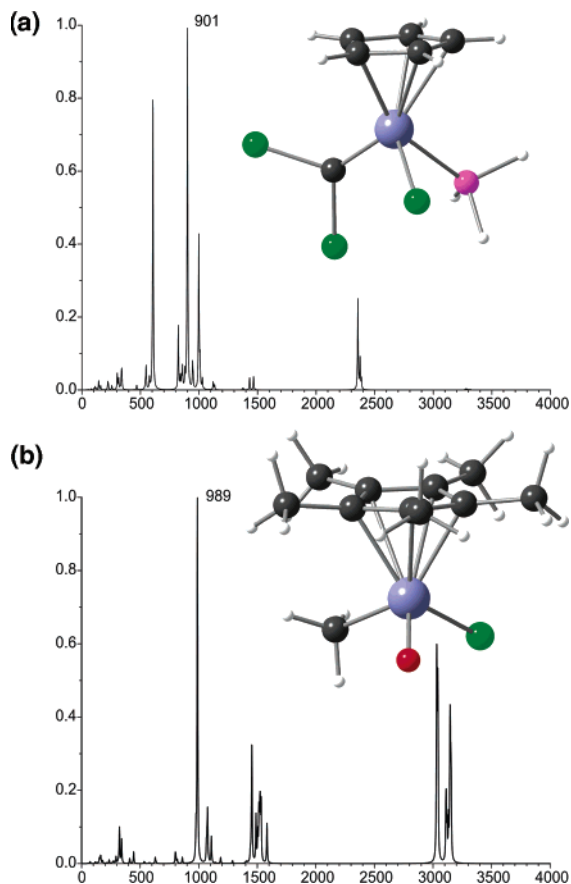


Figure 1. DFT (B3LYP) calculations for the infrared spectrum of (a) (R) - $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CCl}_2)\text{Cl}(\text{PH}_3)$ and (b) (R) - $\text{Re}(\eta^5\text{-Cp}^*)(=\text{O})(\text{CH}_3)\text{Cl}$. The value for the $\text{Os}=\text{C}$ and $\text{Re}=\text{O}$ stretching frequencies (in cm^{-1}) is shown as well.

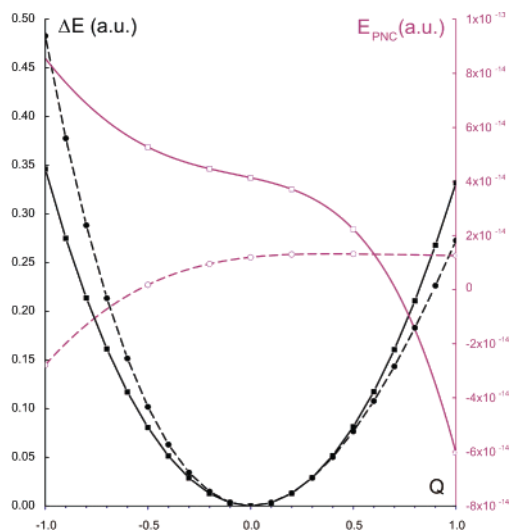


Figure 2. Potential energy curves ΔE (in black) and PNC contributions E_{PNC} along the metal–ligand stretching normal mode Q . All values are in a.u. Solid line, (R) - $\text{Os}(\eta^5\text{-C}_5\text{H}_5)(=\text{CCl}_2)\text{Cl}(\text{PH}_3)$; dashed line, (R) - $\text{Re}(\eta^5\text{-Cp}^*)(=\text{O})(\text{CH}_3)\text{Cl}$.

$\nu_{\text{PNC}}(R; 0 \rightarrow 1) - \nu_{\text{PNC}}(S; 0 \rightarrow 1) = -1.15$ and $+1.09$ Hz for the $\text{Os}=\text{C}$ and $\text{Re}=\text{O}$ stretching modes between the corresponding enantiomers, respectively. This is a 1–2 orders of magnitude improvement over previous results involving C–F stretching modes.^{15,29} The new parity shifts are therefore $\Delta\nu_{\text{PNC}}(R-S)/\nu = -4.3 \times 10^{-14}$ for the $\text{Os}=\text{C}$ and $+3.7 \times 10^{-14}$ for the $\text{Re}=\text{O}$ stretching mode. We mention, however, that the results can be

significantly influenced (even enhanced) through coupling with other modes close to the vibrational transition chosen,³⁰ and for more accurate calculations electron correlation effects should be included as well in the PNC calculations. This, however, would be a formidable task for the compounds discussed here. Nevertheless, our study is a first attempt in identifying suitable heavy element chiral compounds for future PNC measurements.

We finally mention that organometallic compounds could also be useful for PNC studies in high-resolution NMR or Mössbauer spectroscopy, where the natural line-width is sufficiently small. For NMR spectroscopy,²⁰ only heavy metals with nuclear spin $I = 1/2$ are useful to prevent line broadening from nuclear quadrupole coupling. This limits the choice to chiral centers with the isotopes ^{187}Os , ^{183}W , or the lighter isotopes $^{117,119}\text{Sn}$. It may, however, prove to be very difficult to find suitable enantiomers with PNC chemical shift differences beyond a few millihertz.²⁰ For Mössbauer spectroscopy, ^{193}Ir would be a good candidate, where a large number of stable chiral compounds are already known. For PNC effects in electronic transitions, one is restricted to forbidden transitions, such as in luminescence or phosphorescence spectra of heavy metal-containing compounds, which reduces the natural line-width.

Acknowledgment. P.S. is grateful to the Royal Society of New Zealand (Wellington) for granting a James Cook fellowship, and to the Vice-Chancellor Dr. John Hood and Prof. Peter Hunter (Auckland) for making it possible to perform such computer-time-intensive relativistic calculations on a multiprocessor supercomputer.

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