VIP Chiral Metal Complexes

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NWHClI: A Small and Compact Chiral Molecule with Large Parity-Violation Effects in the Vibrational Spectrum**

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Chirality plays a central role in many chemical and biological processes.[1,2] Nature is intrinsically homochiral and, in fact, biomolecular homochirality is one of the many necessary conditions for the existence of life on earth. Whilst the origin of biomolecular homochirality is still the subject of ongoing intense debate,[3] it is well-known that the standard model in physics predicts that parity violation (PV) (or breakdown of mirror-image symmetry) originating from the Z-boson exchange between electrons and nucleons lifts the degeneracy between enantiomers by 10^{-11} kcal mol^{-1} or less, depending on the chiral system involved.[4,5] Despite many attempts to measure these tiny energy differences between enantiomers (and a few irreproducible claims to have actually found them), PV in chiral molecules has never been unambiguously identified by experiment.[6–8] However, over the last 30 years, attempts to measure these effects improved considerably, and now aims at sensitivities of about 0.01 Hz.[9]

The synthesis and enantiomeric purification of thermodynamically stable chiral compounds with enhanced PV effects suitable for spectroscopic measurements currently constitutes one of the most challenging tasks in this field of research.[8,10–12] It is well-known that PV effects scale approximately with Z^5 (Z being the nuclear charge) for electronic and vibrational transitions.[13] This fact implies that chiral molecules with heavy atoms at or close to the center of chirality are the best candidates for the search of large PV effects.[14–16] Moreover, small and compact molecules are ideally suited for such experiments as they provide a more favorable partition function. Another important fact to consider is the operational range of tunable lasers: For example, Chardonnet and co-workers use frequency-stabilized CO_2 lasers in the 878–1108 cm^{-1} range,[6] and a number of heavy-element-containing compounds with vibrational transitions in this range have been investigated in the past by theoretical methods.[10,16–21]

Herein we present a new simple, compact, and yet thermodynamically stable chiral molecule, N≡WHClI, with a parity-violation energy difference in the N–W stretching mode between the enantiomers of 0.71 Hz (2.4×10^{-11} cm^{-1}). The molecule is depicted in Figure 1 together with the simulated vibrational spectrum. The related NWH_3 and NWF_3 molecules have already been detected by Wang and co-workers[22,23] and their vibrational spectra have been analyzed by trapping in solid argon. The fundamental N–W stretching modes are 1092 cm^{-1} for NWH_3 and 1091 cm^{-1} for NWF_3, and thus lie within the desired CO_2 frequency range. At the B3LYP level we obtain the N–W stretching frequencies of 1148 cm^{-1} for N≡WH_3 and 1143 cm^{-1} for N≡WF_3. Therefore, we expect that our B3LYP frequency of 1132 cm^{-1} for N≡WHClI corresponds to an experimental frequency of about 1078 cm^{-1}, thus lying in the correct laser frequency range.

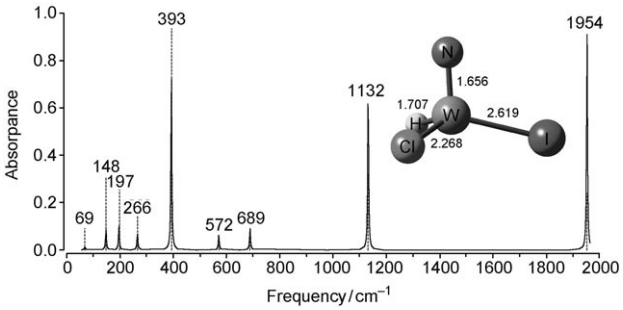
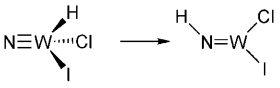


Figure 1. Simulated B3LYP vibrational spectrum of (*R*)-NWHClI. The equilibrium bond lengths are given in Å, and anharmonic frequencies in cm^{-1}.

To discuss the stability of N≡WHClI, we consider a hydrogen shift from tungsten to nitrogen, leading to HN=WClI [Eq. (1)].



(1)

The singlet state of HN=WClI lies 5.8 kcal mol^{-1} above the global minimum of N≡WHClI at the B3LYP level of theory, with an activation energy of 28.7 kcal mol^{-1} for the H-shift; therefore, the barrier is high enough to exclude tunneling. Triplet HN=WClI lies only 0.1 kcal mol^{-1} above the N≡WHClI singlet state, but again with a rather high barrier of 53.0 kcal mol^{-1} to triplet N≡WHClI, which lies

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48.9 kcal mol^{-1} above the corresponding singlet state. Although this near-degeneracy in energy of singlet N≡WHClI and triplet HN=WClI may complicate the synthesis of N≡WHClI, it should not influence the detection of PV effects using tunable lasers, as the N–W stretching mode in HN=WClI is over 100 cm^{-1} smaller than that in N≡WHClI (1011 versus 1132 cm^{-1} at the AVTZ/B3LYP level of theory). Furthermore, at the same level of theory, the dipole moment of triplet HN=WClI is 1.93 D and thus 0.5 D smaller than the value for singlet N≡WHClI (2.44 D). Decomposition pathways to HCl + NWI, HI + NWCl, ClI + NWH, or W + NHClI (considering the most stable spin states) are all endothermic by 77.3, 78.9, 126.3, and 217.4 kcal mol^{-1}, respectively, thus confirming the high thermodynamic stability of NWHClI.

The by far most important individual PV contribution is that of tungsten, which outweighs the second-largest contribution of iodine by a factor of about 30 (B3LYP) and about 50 (LDA). Therefore, the PV energy shift for (*R*)-NWHClI, which is -69 Hz (-2.3×10^{-9} cm^{-1}) at the B3LYP level of theory (see Computational Methods) is completely dominated by the chiral tungsten center. Moreover, the absolute values of E_{PV} are an order of magnitude larger than those for SeOClI investigated recently.[20,21] The PV effects on the fundamental and overtone vibrational transitions for the N–W stretching mode of (*R*)-NWHClI follow the formula $\Delta\nu_{PV}^{0\rightarrow n} = a_1 n + a_2 n^2$ (n is the vibrational quantum number), with $a_1 = 353$ mHz and $a_2 = 2$ mHz at the X2C-B3LYP and $a_1 = 446$ mHz and $a_2 = 4$ mHz at the X2C-LDA level of theory. Therefore the difference $\Delta_{RS}E_{PV}$ between the PV effect on the $0\rightarrow1$ transition for the *R* and *S* enantiomer amounts to 0.71 Hz (2.4×10^{-11} cm^{-1}) at B3LYP level and 0.90 Hz (3.0×10^{-11} cm^{-1}) at LDA level. Thus, these effects exceed previously estimated PV effects for the Se–O stretching mode in SeOClI by a factor of 6–8, and for the C–F stretching mode in CHFBrI[24] by two orders of magnitude. Faglioni and Lazzeretti obtained harmonic frequency shifts in the Hz range for BiHFBr and BiHFI,[25] but these values are in the low-frequency range far below the CO_2 laser line. Thus, N≡WHClI is the most promising candidate to date for the detection of PV in chiral molecules. Moreover, the molecule may also be a good candidate for NMR or UV spectroscopic PV measurements. If synthesis and isolation in solid form proves to be too difficult, the N≡WHClI molecule could be obtained in small amounts in the gas phase, mass-selected, and finally trapped at ultracold temperatures.[26]

Computational Methods

The minimum geometry, vibrational frequencies, and normal modes for all the molecules studied were obtained from density functional theory (DFT) calculations,[27] and the anharmonic frequencies used throughout this work are from a perturbative approach as described in detail by Schaefer et al. and Barone et al.[28,29] For the lighter elements (H, N, Cl) we used all-electron augmented correlation-consistent triple-zeta (AVTZ) Gaussian basis sets,[30–32] whereas for the heavier elements (I, W) AVTZ basis sets together with small-core energy-consistent relativistic pseudopotentials[33,34] were employed. The PV shift to the total electronic energy, E_{PV}, was obtained from Dirac–Hartree–Fock (DHF) and Dirac–Kohn–Sham (DKS) calculations[35] (local density approximation, LDA, and B3LYP[36]) at the optimized geometries. A Gaussian nuclear charge distribution was chosen.[37] For the total number of nucleons, values of 1, 14, 35, 127, and 184 were chosen for H, N, Cl, I, and W, respectively (for details, see reference [8]). For the light elements (H, N), uncontracted Dunning AVTZ basis sets were employed; for the heavier elements (Cl, I, W), we employed Fægri dual-family-type basis sets[38] with additional augmentation functions, that is, 6s3p2d for H, 11s6p3d2f for N, 16s10p5d3f for Cl, 22s19p11d4f3g for I, and 24s22p16d11f4g for W. These four-component DHF and DKS calculations were used to validate the applicability of the two-component relativistic Hamiltonian (X2C)[39] using the AMFI code.[40] These two-component results agree well with the four-component results, with the deviations being in general less than 4%; therefore, for the calculation of the vibrational PV shift, we applied the X2C approximation only. The frequency analysis was carried out with a numerical Numerov–Cooley procedure, which gave the PV-induced frequency shift ν_{PV}^{n} for each state with vibrational quantum number n. The PV contribution to the vibrational transition $n\rightarrow m$ can then easily be calculated as $\Delta\nu_{PV}^{n\rightarrow m} = \nu_{PV}^{m} - \nu_{PV}^{n}$. This local mode analysis contains all the anharmonicity effects along the individual N–W stretching mode, but neglects the coupling between the normal modes. Nevertheless, the anharmonic result (coupling all modes) of $\tilde{\nu} = 1132$ cm^{-1} is in excellent agreement with the one-dimensional anharmonic result of 1134 cm^{-1}, thus indicating that such coupling terms are negligible for this molecule. The PV matrix elements $E_{PV}(q)$ were obtained pointwise along the normal coordinate q of the N–W stretching mode (Figure 2) and subsequently fitted to a polynomial; the outermost points of the resulting potential curve were equivalent to a displacement along the normalized gradient vector of ±0.5 Å. This normal mode almost exclusively describes the change of the N–W distance, and a displacement of 0.5 Å along the normal mode is identical to the elongation of the N–W triple bond by 0.536 Å. For the X2C-HF case, a simple polynomial fit was impractical owing to HF deficiencies in describing the elongation of the N–W bond, which leads to a rather complicated behavior for $q > 0.1$ Å (see Figure 2). For this reason, vibrational PV shifts were obtained at the DFT level only.

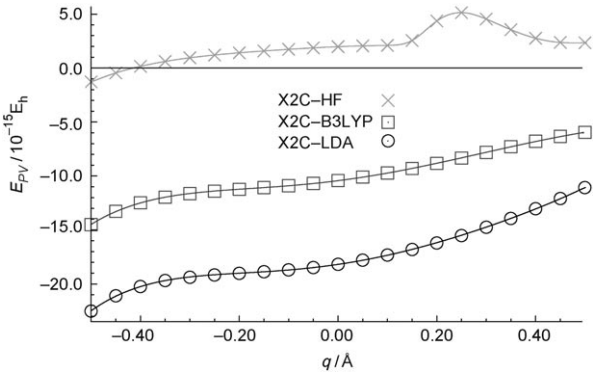

Figure 2. $E_{PV}(q)$ curves along the normalized N–W stretching mode of (*R*)-NWHClI.

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