Mendeleev Commun., 2003, 13(3), 129–130

Parity-violating energy difference between enantiomers: recent developments

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10.1070/MC2003v013n03ABEH001780

Recent theoretical and experimental approaches are critically reviewed.

Parity-violating energy difference (PVED) between enantiomers has been considered as a possible solution for the problem of the origin of homochirality raised by the famous experiment of Pasteur in 1848.[1–4] The term homochirality is used to express that amino acids and sugars in living organisms belong to the L- and D-form, respectively, while in syntheses equal amounts of these enantiomer molecules are produced. The homochirality of biomolecules is accepted as a hallmark of life.[5]

PVED induced by weak nuclear coupling is verified in atoms (reviewed in ref. 6). Calculations of PVED for enantiomeric molecules indicated a very small value of $1\times10^{-17}xkT$, where k is the Boltzman constant, and T is the absolute temperature.[7] Further calculations by Mason, Tranter and MacDermott pointed out that L-amino acids occurring in livings are more stable by this small energy than D-amino acids. Detailed data, including PVED values for sugars, were published.[8]

The 'right sign' of PVED prompted work to find whether the small PVED could push a developing system in the right direction at a bifurcation point.[9] The positive answer of Kondepudi and Nelson has been refuted by Avetisov and Goldanskii.[10]

From 1995 three groups began to perform new calculations of PVED (reviews in refs. 3, 4, 11, 12). They have provided values about one order of magnitude larger than those from previous calculations and confirmed their dependence on the 6th power of the atomic number Z in the asymmetry centre taking relativistic effects into account.[11] The theory also pointed out that the effect of parity violation is even larger in chemical reaction.[13]

Though the new theoretical calculations are more or less consistent, experimental confirmations are necessary. We may divide the experimental approaches into two groups: microscopic and macroscopic measurements. In the first the energy difference is hopefully measured using high-resolution spectroscopic techniques. Lasers,[3] nuclear magnetic resonance (NMR)[14] and the Mössbauer effect[15] were discussed as possible experimental approaches. A Mössbauer experiment performed in collaboration with F. Galsbøl and B. S. Rasmussen from Copenhagen and F. Wagner from Munich on L- and D-tris(1,2-ethanediamine) iridium(III) complex provided only an upper limit of 4×10^{-9} eV being 3.6×10^{2} times larger than PVED.[15] Table 1 containing collected data on possible Mössbauer nuclides is a modified version of that in ref. 15. In the modification PVED values are increased by one order of magnitude and are related to the line centre determined as 10% of the line width. It is seen that the best candidate for a successful study is the $^{181}_{73}$Ta nuclide. However, note that calculations how PVED appears in the isomer shift of a Mössbauer line are not known.

In Mössbauer measurements on chiral iron complexes a difference of $(1.9\pm1.0)\times10^{-10}$ eV was found.[16] The difference does not seem statistically significant; thus, it should be considered only as an upper limit for PVED. According to Table 1, this upper limit is $\approx10^{4}\times$PVED. In this measurement, however, the difference was 2%, five times less than the conservative estimate of 10% of the line width in Table 1. Thus, a Mössbauer study on Ta-containing complexes *via* the $^{181}_{73}$Ta nuclide is worthwhile even accepting that working with this nuclide is difficult.

Sophisticated infrared spectroscopy on the vibrational modes of CHFClBr enantiomers has shown an upper limit for the difference of 13 Hz, while the theory predicted 2 mHz.[17] Another high-resolution spectroscopic technique NMR was also considered as a possible way to measure PVED directly.[14] Robert and Barra[14] concluded that the difference could be measured with an ultra-high-resolution technique in the cases of high Z value spin one half nuclei such as Pt, Tl, Xe in the asymmetry centre of the enantiomers.

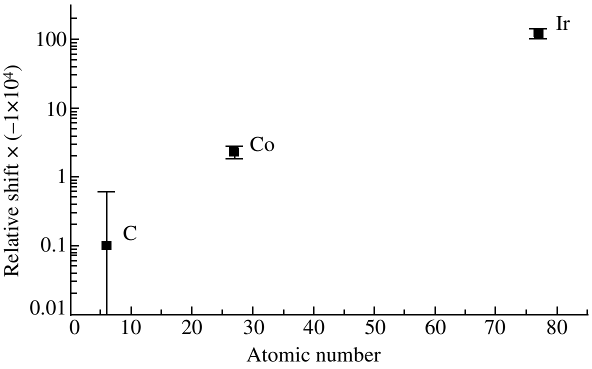

Figure 1 Relative shifts of the distribution of crystallisations depending on the atomic number of the atom in the asymmetry centre (after ref. 20).

Presently, suitable microscopic or, in other words, direct methods to measure PVED are only in future plans; therefore, macroscopic or indirect methods may be used at least to demonstrate the theoretically forecasted PVED. Macroscopic methods, like polymerization or crystallization of enantiomers, amplify the small differences[18,19] and simulate the mode how could PVED generate asymmetry during chemical evolution. In our approach, we dealt with the crystallization of a racemic mixture of L- and D-forms of sodium ammonium tartrate, tris(1,2-ethanediamine)cobalt(III) or tris(1,2-ethanediamine)-iridium(III) complexes.[20] Performing a large number of crystallizations, the distribution of the circular dichroism of dissolved crystallites was shifted from a zero value for Co and Ir complexes outside error while the distribution for tartrate crystallization did not show a shift larger than the error (Figure 1). This study appears to have provided an experimental demonstration of parity-violating weak interactions in molecules. According to the main critics of such macroscopic experiments, it is questionable whether the preferential crystallization is due to the parity-violating weak interaction or to some unknown impurities.[3] This reasoning runs into trouble because in our experiments different controls were performed[20] and, in addition, the influence of 'suspected' impurities surely did not increase with atomic number as was found experimentally (Figure 1) and expected from the theory. In spite of this result, we consider PVED as the determining agent for the origin of

Table 1 Mössbauer nuclides for the possible measurement of parity-violating energy difference (PVED). Central value means 10% of line width.

Nuclide	γ-energy/ keV	Linewidth Γ/eV	Putative PVED/eV	PVED/ central value
$^{181}_{73}$Ta	6.23	1.3×10^{-10}	8.1×10^{-12}	6.2×10^{-1}
$^{73}_{32}$Ge	13.3	2.7×10^{-11}	6.0×10^{-14}	2.2×10^{-2}
$^{237}_{93}$Np	59.6	1.4×10^{-8}	3.5×10^{-11}	2.5×10^{-2}
$^{193}_{77}$Ir	73.0	2.6×10^{-8}	1.1×10^{-11}	4.2×10^{-3}
$^{67}_{30}$Zn	93.3	9.3×10^{-11}	3.9×10^{-14}	4.2×10^{-3}
$^{57}_{26}$Fe	14.4	9.6×10^{-9}	1.5×10^{-14}	1.5×10^{-5}

homochirality as an open question. On the other hand, the idea of the universal unity of the effects of parity violation in the inanimate and living worlds is philosophically attractive. Consequently, efforts in this direction should be continued.

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Received: 25th April 2003; Com. 03/2106