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SeOClI: A promising candidate for the detection of parity violation in chiral molecules

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Parity violation (PV) effects at the Dirac-Hartree-Fock and Dirac-Kohn-Sham level of theory are presented for the chiral molecule SeOClI. The PV energy contribution to the S enantiomer of SeOClI ranges between −7.1 and −9.2 Hz, depending on the level of theory applied. For the Se-O fundamental stretching mode, which lies within the CO_2 laser frequency range, we obtain PV energy differences of 110 mHz between the two enantiomers, which is twice as large compared to the previously investigated C-F stretching mode of CHFBrI.

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I. INTRODUCTION

Although it is well accepted that the standard model predicts that parity violation (PV) originating from the weak neutral current between electrons and nucleons introduces a tiny energy difference between mirror image molecules (enantiomers) of a chiral compound [1–4], it has never been unambiguously observed experimentally [5,6], despite many claims in the past [7–10]. As PV energy differences are currently estimated to be well below the 1 Hz range for most spectroscopic properties of suitable molecules [11], the search for thermodynamically stable chiral compounds with large parity violation effects, together with the development of ultrahigh-resolution spectroscopic techniques, constitutes one of the most exciting and challenging areas in current molecular physics [11–13].

One very promising future experimental method is to trap molecules at ultracold temperatures (in the millikelvin range or below) [14], for example by pulsed electric fields [15,16], and subsequently perform ultrahigh-resolution spectroscopic measurements of vibrational or electronic transitions. Tunable lasers for high-resolution measurements are already available in the 1–20 μm range, which can reach accuracies below the 1 Hz range [5,17–19]. In such experiments, PV can be detected if the resolution is smaller than the difference between the frequencies of the R and S isomers of a chiral compound, $\Delta\nu_{PV}^{RS}=\nu^R-\nu^S$. To facilitate future measurements, a chiral compound should meet the following requirements. First, as PV effects roughly scale as Z^5 [20,21], Z being the nuclear charge, systems with heavy atoms as chiral centers or heavy atoms directly neighboring chiral centers [22–24] are ideal candidates. Second, because of the single-center theorem of Hegstrom and co-workers [25], it is desirable to involve two or more neighboring heavy elements in the chiral compound with PV contributions of the same sign such that they amplify. Third, these compounds should consist of as few atoms as possible leading to a more favorable partition function. Fourth, the vibrational frequency should be in the desirable laser frequency range, for example in the 878–1108 cm^{-1} range if a tunable frequency-stabilized CO_2 laser is used [17]. Fifth, concerning electronic transitions, the natural line broadening should be small enough to obtain high resolution, thus restricting transitions approximately to the greater than millisecond range lifetimes. Sixth, the compound must be reasonably stable and synthesizable, preferably on the scale of some grams, but gas phase synthesis and mass-selected separation from by-products is also a possibility. And seventh, enantioselective synthesis or enantiomeric enrichment is highly desirable for independent mesurements.

Electroweak interactions in simple chiral molecules have been investigated before, but if heavy central atoms are involved, they are often not thermodynamically stable [26,27]. Here we present a simple, chiral, and thermodynamically stable molecule involving heavy elements, where atomic PV contributions between the two most heavy elements do not cancel out, the SeOClI molecule (Fig. 1). This molecule meets most of the conditions mentioned. The vibrational frequencies of the Se-O stretching modes of all experimentally known molecules in this class ($SeOF_2$, $SeOCl_2$, $SeOBr_2$, SeOClF, and SeOBrCl) lie in the range of 950–1050 cm^{-1} [28–30]. Furthermore, $SeOCl_2$ is used as a polar solvent and thus is readily available as a possible precursor for the synthesis of SeOClI.

II. METHOD

The minimum geometry (Fig. 1) and harmonic frequencies of SeOClI were obtained from scalar relativistic density functional theory (DFT) calculations [31] employing Becke's three-parameter hybrid functional (B3LYP) [32] which contains exact exchange. For the lighter elements (O, Cl) all-electron augmented correlation-consistent valence triple-ζ (AVTZ) Gaussian basis sets were used [33–35], while for the heavier elements (Se, I) AVTZ basis sets in connection with small-core energy-consistent pseudopotentials [36] were employed. The optimized distances R_{SeO}, R_{SeCl}, and R_{SeI} are 1.609, 2.251, and 2.632 Å, respectively; the former distances agree quite well with the experimental equlibrium distances of 1.612 (R_{SeO}) and 2.204 Å (R_{SeCl}) for the $SeOCl_2$ molecule [37]. The calculated angles are 106.2° for $\angle_{OSeCl}$, 107.0° for $\angle_{OSeI}$, and 99.5° for $\angle_{ClSeI}$.

The PV contribution to the total electronic energy, E_{PV}, was obtained from all-electron Dirac-Hartree-Fock (DHF)

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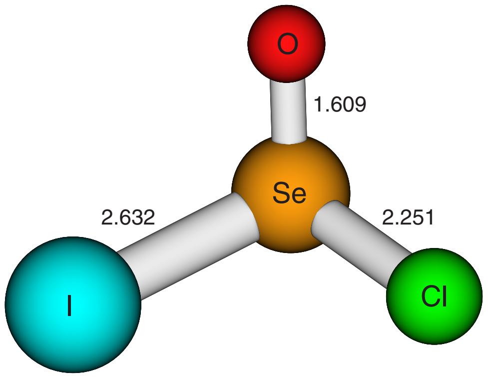

FIG. 1. (Color online) The *S* enantiomer of SeOClI (the lone electron pair of Se points away from the reader). The equilibrium bond lengths are given in angstroms.

or Dirac-Kohn-Sham (DKS) calculations [local density approximation (LDA) and B3LYP] [38] using uncontracted dual-family-type Gaussian basis sets of augmented triple- to quadruple-ζ quality. These basis sets are based on Dunning's AVTZ basis sets for the light atoms (O, Cl) converted to dual type, and on Faegri's dual family basis sets [39], which were augmented. This resulted in uncontracted basis sets of $11s6p4d3f$ for O, $16s10p5d3f$ for Cl, $20s17p11d4f2g$ for Se, and $22s19p11d4f3g$ for I.

The important part of the parity-violating contribution is expressed by the (nuclear-spin-independent) *P*-odd operator [40–42]

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

$G_F = 2.222\,55 \times 10^{-14}$ a.u. is the Fermi coupling constant, γ^5 the pseudoscalar chirality operator, and the summation is taken over all electrons i and nuclei n. Gaussian nuclear charge distributions were chosen for the particle densities with nuclear radii taken from ϱ_n [43]. 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. The Weinberg mixing angle θ_W was chosen such that $\sin^2\theta_W = 0.2319$, and for the total number of nucleons $A_n = N_n + Z_n$ values of 16, 35, 79, and 127 have been used for O, Cl, Se, and I, respectively. The energy difference between the two enantiomers is $\Delta_{RS}E_{\mathrm{PV}} = 2E_{\mathrm{PV}}$, and the parity-violating energy shift E_{PV} is obtained from the expectation value of H_{PV} at the DHF or DKS level of theory.

TABLE I. Dipole moments μ (in debye) and parity-violating contributions E_{PV} (in atomic units) for each atom at the equilibrium geometry of *S*-SeOClI.

Atom	DHF	DKS LDA	DKS B3LYP
μ	2.889	2.019	2.264
Se	-3.541×10^{-16}	-3.945×10^{-16}	-3.964×10^{-16}
O	2.770×10^{-18}	2.860×10^{-18}	3.054×10^{-18}
Cl	-2.084×10^{-18}	4.510×10^{-18}	2.330×10^{-19}
I	-1.041×10^{-15}	-6.943×10^{-16}	-7.964×10^{-16}
Total (a.u.)	-1.394×10^{-15}	-1.082×10^{-15}	-1.190×10^{-15}
Total (Hz)	-9.17	-7.12	-7.83

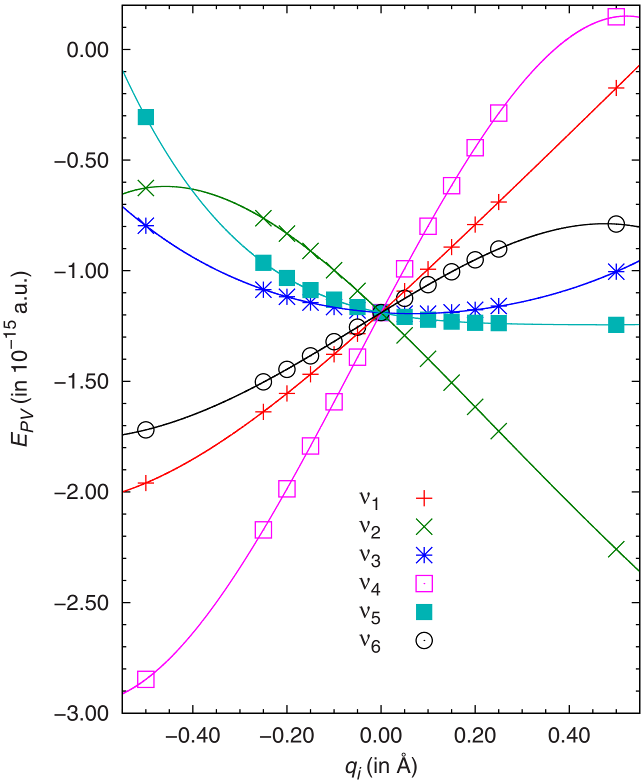

FIG. 2. (Color online) $E_{\mathrm{PV}}(q_i)$ along all six normal modes of *S*-SeOClI.

The parity-violating matrix elements $E_{\mathrm{PV}}(q_i)$ were calculated pointwise along the potential energy curve $V(q_i)$ and fitted to a polynomial along the normal coordinate q_i for a specific vibrational mode i. The outermost points of the potential curves were equivalent to a displacement along the normalized gradient vector of ±0.5 Å. The frequency analysis was carried out through a numerical Numerov-Cooley procedure, which gave the PV-induced frequency shift ν_{PV}^n as the following expectation value:

$$\nu_{\mathrm{PV}}^n = \langle \Psi_n(q_i) | E_{\mathrm{PV}}(q_i) | \Psi_n(q_i) \rangle, \tag{2}$$

with Ψ_n being the vibrational wave function of the state with vibrational quantum number n. The PV contribution to the vibrational transition $n \rightarrow m$ can then easily be calculated as $\Delta\nu_{\mathrm{PV}}^{n\rightarrow m} = \nu_{\mathrm{PV}}^m - \nu_{\mathrm{PV}}^n$.

III. DISCUSSION

SeOClI is a nonplanar closed shell molecule, with the barrier to inversion being 1.06 eV and thus high enough to prevent interconversion (tunneling) between the different enantiomers of SeOClI. Hence SeOClI is chiral at the experimental time scale. It also has a rather large dipole moment of about 2.264 D at the B3LYP level of theory [see Table I; a

TABLE II. Calculated harmonic vibrational frequencies ω, corresponding fundamental vibrational transitions ν (in cm^{-1}), from an anharmonic analysis at the B3LYP level of theory, and PV-induced frequency shifts $\Delta\nu_{\text{PV}}$ (in millihertz) to the vibrational transitions $(n=0\rightarrow m)$ at the DKS B3LYP level of theory for all six modes of *S*-SeOClI.

	Mode	ω	ν	$0\rightarrow1$	$0\rightarrow2$	$0\rightarrow3$	$0\rightarrow4$	$0\rightarrow5$
ν_1	Se-O stretch	978	968	−55.5	−110.6	−165.4	−219.7	−273.6
ν_2	Se-Cl stretch	346	357	−3.5	−6.9	−10.1	−13.2	−16.2
ν_3	Se-I stretch	246	245	−55.4	−105.4	−150.3	−190.5	−226.2
ν_4	O-Se-Cl bend	237	235	−40.6	−81.3	−122.1	−163.0	−204.1
ν_5	O-Se-I bend	167	166	112.4	230.2	351.6	474.5	596.6
ν_6	Cl-Se-I bend	100	99	−55.2	−121.6	−197.9	−282.1	−371.3

more accurate coupled-cluster singles-doubles with perturbative triples calculation, CCSD(T), gives 2.494 D], which is useful information for future trapping of this molecule. Furthermore, the Se-I bond is reasonably stable with a dissociation energy of 1.31 eV at the B3LYP level of theory. In addition, ligand scrambling to $\text{SeOCl}_2+\text{SeOI}_2$ is unlikely for entropy reasons as this system is only 0.02 eV more stable compared to two molecules of SeOClI.

The parity-violation energy contributions $E_{PV}(q_i)$ for a specific local mode i are shown in Fig. 2. Our local mode analysis contains all the anharmonicity effects along the individual modes, but neglects the coupling between the normal modes. Whereas the inclusion of the coupling between different normal modes is important for the ν_2 mode due to Fermi resonance with the $\nu_3+\nu_6$ combination band (obtained from an anharmonic vibrational analysis in normal modes which includes all coupling terms in the cubic and quartic force fields; see Table II), the important Se-O stretching mode with a frequency of 968 cm^{-1}, which lies in the CO_2 laser frequency range, nevertheless is well separated from all the other modes and thus justifies a local mode treatment, in contrast to other chiral molecules [44–46].

The calculated PV energy contributions for *S*-SeOClI are shown in Table I. E_{PV} is nearly completely accounted for by the individual PV energies for the two heaviest elements Se and I. In addition, the contribution of I is about 2–3 times larger than the Se contribution and thus accounts for 65–75 % of the total E_{PV}. Unlike in previous cases where the most important atomic PV contributions between different elements have different signs and can almost cancel out [47], the sign of E_{PV} for Se and I remains the same for all methods applied. Moreover, the DHF and LDA values are very similar, and we expect that other density functionals or high-level *ab initio* calculations, such as a coupled cluster treatment [48], will yield results close to the ones reported here.

Table II shows the results for the fundamental and overtone vibrational transitions up to $n=5$ for all six modes of *S*-SeOClI. As found in earlier work on the parity violation effects in the C-F stretching mode [23,47,49], the relation $\Delta\nu_{\text{PV}}^{0\rightarrow m}\approx m\Delta\nu_{\text{PV}}^{0\rightarrow1}$ holds reasonably well for the stretching modes and the O-Se-Cl bending mode; the remaining bending modes exhibit a less regular behavior. The ν_5 O-Se-I bending mode has the largest PV contribution; however, the fundamental frequency at 166 cm^{-1} is rather low and may not be so easily accessible for high-resolution spectroscopy. Nevertheless, with a difference of $\Delta_{RS}E_{\text{PV}}=110$ mHz at the B3LYP level of theory (the similar values of 126 mHz at the LDA and 136 mHz at the HF level show the consistency of our results and the accuracy of our prediction) between the PV contributions of the *R* and *S* enantiomers for the fundamental vibrational transition of the Se-O stretching mode, which lies in the experimentally desirable range of $\sim$1000 cm^{-1}, SeOClI exhibits PV effects twice as large as CHFBrI for the C-F stretching mode. Moreover, the ^{77}Se isotope has nuclear spin 1/2 and is ideally suited for gas phase NMR measurements. For this purpose the PV contribution for the ^{77}Se nuclear magnetic shielding tensor using the nuclear-spin-dependent PV Hamiltonian as described in Refs. [50–53] needs to be determined, which is part of our future work. To conclude, SeOClI is a promising candidate for the detection of parity violating effects in chiral molecules.

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