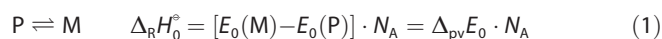


Tunneling and Parity Violation in Trisulfane (HSSSH): An Almost Ideal Molecule for Detecting Parity Violation in Chiral Molecules

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Measuring the parity-violating energy difference $\Delta_{\text{pv}}E$ between the enantiomers of chiral molecules is a major challenge of current physical-chemical stereochemistry. An important step towards this goal is to identify suitable molecules for such experiments by means of theory. This step has been made by calculations for the complex dynamics of tunneling and electro-weak quantum chemistry of parity violation in the “classic” molecule trisulfane, HSSSH, which satisfies the relevant conditions for experiments almost ideally, as the molecule is comparatively simple and parity violation clearly dominates over tunneling in the ground state. At the same time, the barrier for stereomutation is easily overcome by the S–H infrared chromophore.

The physical-chemical foundations of molecular chirality are among the central questions of stereochemistry.^[1] According to the traditional view, consistent with the framework of ordinary quantum chemistry retaining only the electromagnetic force, by symmetry the two enantiomers of chiral molecules (say P and M for axial chirality) are energetically exactly equivalent corresponding to an exactly vanishing reaction enthalpy $\Delta_{\text{R}}H_0^\circ=0$ for the stereomutation reaction (1). This symmetry is related to the exact conservation of the quantum number parity (+1 or –1) in physics, which indicates the symmetry of the wave function with respect to space inversion (+ for symmetric, – for antisymmetric). With the discovery of parity non-conservation (or “violation”) in nuclear and elementary particle physics in 1956/57 and the inclusion of the weak nuclear force in “electroweak quantum chemistry” (see Ref. [2] and the references therein), theory predicts a small “parity violating” energy difference $\Delta_{\text{pv}}E_0$ corresponding to a nonzero reaction enthalpy for Equation (1) (see also Figure 1):



where $E_0(\text{M})$ and $E_0(\text{P})$ are the ground state energies of the enantiomers and N_{A} is the Avogadro constant. Early quantitative calculations existed from about 1980,^[3] giving exceedingly small (“immeasurable”) absolute values for $\Delta_{\text{pv}}E$ (see also Ref. [1] for the early work). More recent theory, starting with re-

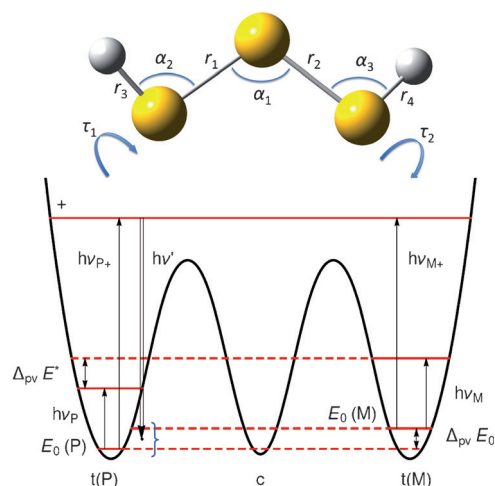


Figure 1. Definition of the internal coordinates of HSSSH and possible experimental schemes to measure parity violating energy differences (see text for further explanation).

sults from our group in 1995/96, resulted in a major predicted increase of $\Delta_{\text{pv}}E$ by one or two orders of magnitude for typical benchmark molecules. This increase has been confirmed by many groups and theory seems to be consistent and well established now (reviewed in Refs. [2,4–7]). However, so far no successful experiment has been reported on molecular parity violation. Such experiments are among the major challenges of current physical-chemical stereochemistry. They are of crucial importance for several reasons: 1) to provide a fundamental check on current theory, 2) to allow for detailed theoretical analysis, which can contribute independent information on fundamental parameters of the standard model of particle physics (SMPP, see Ref. [2]), 3) to contribute to an understanding of the long-standing unsolved question of the origin of biomolecular homochirality, where molecular parity violation is possibly (but not necessarily) important (see Refs. [8,9]).

Of several proposed experimental approaches (reviewed and critically discussed in Refs. [2,9]), only two variants are currently pursued. They can both be understood qualitatively with the scheme shown in Figure 1. The first proposal, due to Letokhov, was to measure a frequency difference between corresponding absorption lines of the two stable enantiomers (say, in the infrared spectrum of $\text{CHFClBr}^{[10]}$). In Figure 1, this would correspond to measuring the difference $(h\nu_{\text{M}} - h\nu_{\text{P}}) = (\Delta_{\text{pv}}E^* - \Delta_{\text{pv}}E_0)$, thus a difference of parity violating energy differences $\Delta_{\text{pv}}E$ in different levels of the molecule (we use the notation $\Delta_{\text{pv}}E$ when no particular level is specified). Current experimental and theoretical work along these lines has been re-

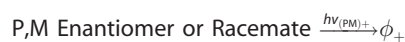
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viewed in Refs. [2,5,6,9,11]. While so far not successful, it seems possible that such experiments will be successful relatively soon for chiral molecules with very heavy atoms, for which relatively large ($\Delta_{pv}E^* - \Delta_{pv}E_0$) are predicted because of the rough scaling with the fifth power Z^5 of nuclear charge Z . Given current experimental capabilities,^[11] an important requirement will be the enantiopure synthesis of appropriate molecules. We shall not discuss this approach any further here.

Another approach, proposed in Ref. [12], relies on the use of an intermediate spectroscopic level of well-defined parity (labelled + in Figure 1). Such a level has allowed spectroscopic transitions to the ground states of both enantiomers, and thus, $\Delta_{pv}E_0$ can be measured directly and individually by the spectroscopic "combination difference" ($h\nu_{P,+} - h\nu_{M,+}$) in a "static" spectroscopic experiment.^[11,12] An interesting time-dependent realization of this experiment uses the spectroscopic properties of this scheme to obtain $\Delta_{pv}E$ by means of the observation of the time dependence of parity in the following sequence of steps^[12] (Figure 2):

1. Selection of parity in the excited state:



2. Preparation of a state of well-defined parity in the ground (low-energy) state:



This state of well-defined parity is not an energy eigenstate of the molecule but a superposition of the eigenstates with energies $E_0(M)$ and $E_0(P)$, which thus depends on time according to Figure 2.

3. Sensitive detection of the probability to find the initially absent parity (+) in the prepared lower energy state [Eq. (2)]:

$$p_+ = 1 - p_- = \sin^2(\pi \cdot \Delta_{pv}E \cdot t/h) \approx (\pi \cdot \Delta_{pv}E \cdot t/h)^2 \text{ (small } t) \quad (2)$$

This detection uses again the spectroscopic selection rules, which result in a line spectrum evolving in time, where the allowed "+" lines are initially absent but increase in intensity following Equation (2). The experiment has to be carried out in

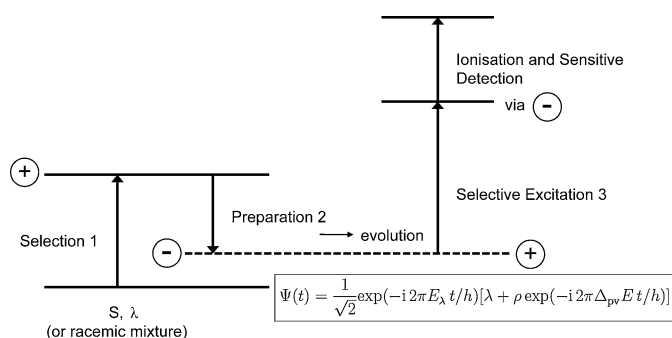


Figure 2. Scheme of the time-dependent experiment to measure $\Delta_{pv}E$.^[9,12]

the absence of external perturbations, for instance, in a molecular beam. In this case, the free flight distance Δx in the beam can be used as a clock being related to the evolution time t by the molecular velocity v in the beam $t = \Delta x/v$. A recent experimental setup has been tested along these lines with the simple achiral molecule NH_3 (seeded in a beam with Ar), providing very sensitive detection over a flight distance of about 1 m, corresponding to flight times of about 2 ms.^[13] From this and Equation (2), combined with the relevant detection sensitivity, one can estimate that $\Delta_{pv}E$ is on the order of 100 aeV [or about $(hc) \times 10^{-12} \text{ cm}^{-1}$ corresponding to $\Delta_R H_0^\circ = 10^{-11} \text{ J mol}^{-1}$] and will lead to detectable signals over this flight distance. Such values for $\Delta_{pv}E$ can be found for chiral molecules involving "light" atoms no heavier than sulfur and chlorine,^[14] which is one advantage of this approach. Another advantage is that there is no need for syntheses of pure enantiomers, one can work with a racemic mixture. One might say that the approach relies on the elegant in situ synthesis (in the beam) of a pure "parity isomer (χ_-) of the chiral molecule", which in itself is an interesting concept corresponding to a rather special molecular state not previously prepared for stable chiral molecules.

The intermediate excited state could be an achiral electronically excited state as in difluoroallene, for instance.^[11,12,15] It can also be an excited vibrational state if the barrier for interconversion is small (for instance about 1000 cm^{-1} in ClOOC^\ddagger ^[7,16]), and the corresponding state is near or above the barrier as is also indicated in Figure 1. We also note for clarity that the prepared low-energy state (χ_-) is not usually exactly the ground state but could be an excited rotational or low-energy vibrational state, which is initially not populated thermally, but well below the barrier (in the case of NH_3 an excited rotational state of well-defined parity in a cold molecular beam was prepared^[13]).

An important first step in the multistep^[9] approach to realize such an experiment is the selection of an appropriate molecule. A first requirement is that the tunneling splitting ΔE_\pm for interconverting the enantiomers must be much smaller than the parity violating energy difference [Eq. (3)]:

$$\Delta E_\pm \ll \Delta_{pv}E_0 \quad (3)$$

Indeed, Equation (3) is a requirement for an energy level scheme as in Figure 1 with the localized enantiomeric eigenstates to be meaningful at all. Technically one replaces $\Delta_{pv}E_0$ by the parity violating potential difference $\Delta_{pv}E_{el}$ at the chiral equilibrium geometry, which is directly obtained from electro-weak quantum chemistry^[2,7] and of the same order as $\Delta_{pv}E_0$ (see below). In practice, the requirement in Equation (3) is satisfied for all chiral molecules that can be prepared as stable enantiomers, but it is often not satisfied for simple molecules that might appear as most appropriate candidates for the experiment. For instance, hydrogen peroxide, HOOH , as well as HSSH do not satisfy this requirement (ΔE_\pm is on the order of 10 cm^{-1} for HOOH). On the other hand, ClOOC^\ddagger and ClSSCI do satisfy Equation (3).^[14,16] However, the excited states with well-defined parity in Figure 1 must be accessible to currently available laser excitation, which is not the case for these molecules.

Also, the spectroscopic complexity must be small, chiral molecules with a minimum of four atoms would be ideal and an otherwise quite suitable molecule such as dichloroallene with five non-hydrogen (and a total of seven) atoms is already borderline for a successful implementation of the experiment, although the magnitude of the parity violation for this molecule would be sufficient. For simpler chiral structures investigated over the last years in our group, and proven as theoretically suitable candidates for the experiment, no method of preparation could be found in spite of extended attempts, all unsuccessful. Thus the identification of a suitable, simple chiral molecule that can be prepared in the laboratory is at present a truly crucial aspect of this approach to molecular parity violation.

We have in the present theoretical work found that trisulfane, HSSSH (Figure 1), satisfies the requirements almost ideally. Polysulfanes, while not very stable, have been known as textbook examples of accessible polysulfur compounds for a long time.^[17] Trisulfane as well as HOOOH have been studied by ab initio theory^[18,19] and spectroscopy^[20–22] in different contexts (see also Ref. [23]). However, parity violation in relation to tunneling has so far escaped notice and we report here the corresponding, very favorable results.

To estimate the values of $\Delta_{\text{pv}}E$ and ΔE_{\pm} , we performed both electronic structure and nuclear motion computations. Equilibrium geometries and transition state structures for the tunneling motion are summarized in Figure 3. Further data are given in the Supporting Information (SI) in detail, where we also describe the computational methods. Figure 3 clearly shows that

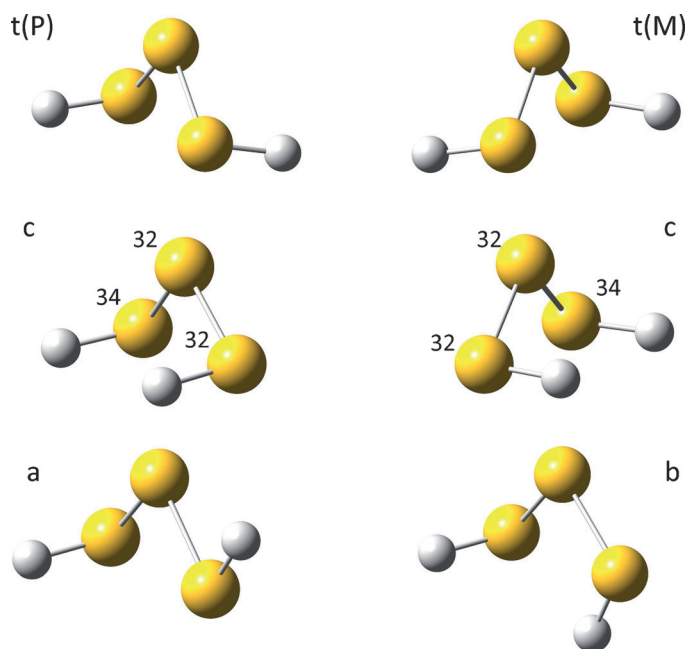


Figure 3. Structures corresponding to the stationary points of HSSSH: *trans*-like equilibrium structures (marked by *t*(P) for the P isomer and *t*(M) for the M isomer, chiral), *cis*-like equilibrium structures (marked by *c*, achiral for HSSSH and chiral for HSS³⁴SH as shown in this figure), first-order saddle point of lower energy (marked by *a*), first-order saddle point of higher energy (marked by *b*). For the main isotope ³²S, we use the symbol S for simplicity.

HSSSH has chiral *trans*-like structures (marked by *t*, the two enantiomers being distinguished by the *P/M* terminology of axially chiral molecules^[24]) and achiral *cis*-like equilibrium structures (marked by *c* in Figure 3), the latter being slightly higher in energy. The *trans*- and *cis*-like structures are connected by two first-order saddle points (with structures marked by *a* and *b* in Figure 3). Both barriers against the interconversion of the *trans*- and *cis*-like structures are higher than 2000 cm⁻¹. If one of the outer sulfur atoms (we use S for the main isotope ³²S) is replaced by ³⁴S, the *cis* structures are isotopically chiral (Figure 3, middle, see also Refs. [1,25]).

Since HSSSH is a double rotor possessing two torsional degrees of freedom, a 2D torsional potential energy surface (PES) was calculated as a function of the τ_1 and τ_2 HSSS torsional angles. Our calculations, described in the SI in detail, result in the very interesting two-dimensional potential energy function $V(\tau_1, \tau_2)$ shown in Figure 4. This potential indicates that direct tunneling from *t*(P) to *t*(M) through the diagonal with the high “mountain” at $\tau_1 = \tau_2 = 180^\circ$ is unlikely and a sequential path via the *cis* structures is favorable with low saddle points marked “*a*” in Figure 4.

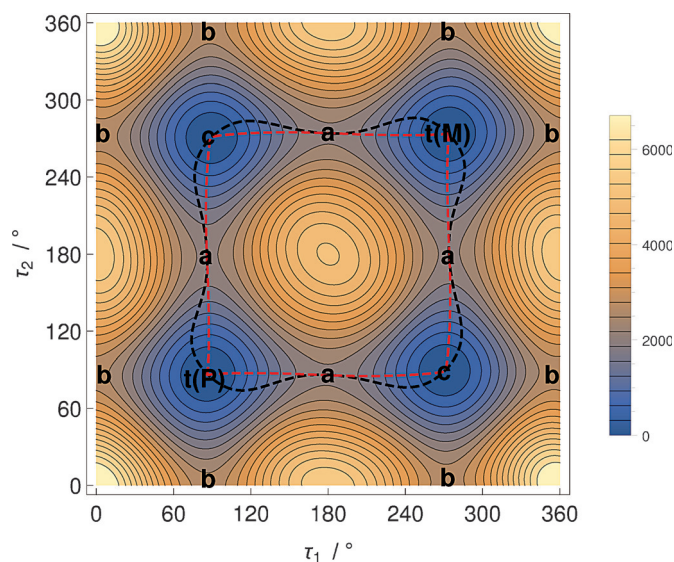


Figure 4. Contour plot of the 2D $V(\tau_1, \tau_2)$ potential energy surface. Equilibrium structures *t*(P), *t*(M) and *c* and first-order saddle points (*a* and *b*) are explicitly marked. The 1D flip-flop and the IRC paths are denoted by the black dashed and red dashed lines. The difference between two equipotential lines corresponds to $V/(hc) = 310 \text{ cm}^{-1}$, equivalent to 3.71 kJ mol^{-1} .

In addition to the 2D torsional treatment, we also selected two 1D paths to describe the tunneling dynamics of HSSSH. First, a “circular” 1D minimum energy path (see the black dashed line in Figure 4) connecting the four equilibrium structures was generated from the 2D PES. This path is similar to the 1D flip-flop path of Ref. [18] (for HOOOH) and connects the two *trans*-like [*t*(P) and *t*(M)] and two *cis*-like (*c*) equilibrium structures through the four lower energy first-order saddle points (*a*). Second, we also examined the intrinsic reaction coordinate (IRC) path (see the red dashed line in Figure 4 and the SI for details).

The chiral *trans*-like equilibrium structure is predicted to be energetically lower in the \tilde{X}^1A ground state of HSSSH by 39 cm^{-1} at the MP2/cc-pVTZ level of theory, and by 23 cm^{-1} at the CCSD(T)/cc-pVQZ level of theory in comparison to the *cis*-like equilibrium structure. Upon extrapolation to the complete basis set limit, the difference is obtained to be 11 cm^{-1} , and after the inclusion of zero-point vibrational energy only 3 cm^{-1} . Therefore, the *trans*- and *cis*-like equilibrium structures are energetically almost equivalent. After the extrapolation to the complete basis set limit, transition state (a) is found at 2290 cm^{-1} above the potential minimum, and transition state (b) lies 2850 cm^{-1} above the potential minimum. Including zero point energy for the lowest quasi-adiabatic channel,^[26] one finds 2253 cm^{-1} for (a) and 2809 cm^{-1} for (b). We note that there are three further planar structures ($\tau_1 = \tau_2 = 180^\circ$ at 5200 cm^{-1} , center in Figure 4), ($\tau_1 = 180^\circ$, $\tau_2 = 0^\circ$ at 5740 cm^{-1}) and ($\tau_1 = \tau_2 = 0^\circ$ at 6970 cm^{-1}), which are second-order saddle points. We also checked the S–H inversion as a possibly competing pathway to torsion. This barrier for inversion was computed to be at 24750 cm^{-1} with respect to the potential minimum, and thus too high to be relevant for the dynamics considered here.

The parity-conserving electronic (V) and parity-violating potentials (E_{pv}) along the IRC path are given in Figure 5 (see SI for details). The IRC path, as depicted in Figure 5, connects the $t(P)$ and $t(M)$ *trans*-like chiral equilibrium structures through the transition structures (a) and *cis*-like equilibrium structures. As can be seen from Figure 5, the P-enantiomer is stabilized with respect to the M-enantiomer, the computed $E_{pv}(P\text{--HSSSH})$ value is $(hc) \times (-8.03 \times 10^{-13})\text{ cm}^{-1}$. The signed electronic parity-

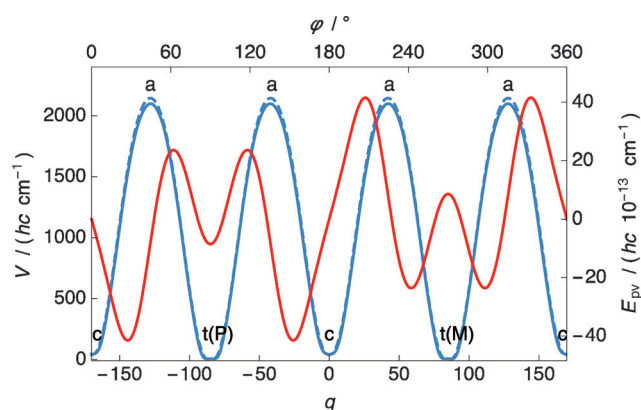


Figure 5. Potential energy function corresponding to the 1D IRC reaction path (left-hand ordinate scale, see the text for discussion). The electronic Born–Oppenheimer (dashed blue line) and lowest quasi-adiabatic channel potentials (solid blue line) are indicated, both being referred to their respective minima, which are separated by the 8D zero point energy $(hc) 4389\text{ cm}^{-1}$. Equilibrium structures [$t(P)$, $t(M)$ and c] and lower energy first-order saddle points (a) are explicitly marked. The parity-violating potential E_{pv} is given by the red line (right-hand ordinate scale). The dimensionless reaction coordinate q is defined by the numbered structure points given in the SI and the polar angle φ can be defined in terms of the τ_1 and τ_2 torsional angles (Figure 4). The smooth functions were obtained by either interpolation (Born–Oppenheimer and lowest quasi-adiabatic channel potentials) or Fourier series fit (parity-violating potential) of the computed discrete points.

violating energy difference $\Delta_{pv}E_{el}$ between the two enantiomers is defined as the difference [Eq. (4)]:

$$\Delta_{pv}E_{el}(q_e) = E_{pv}^{el}(q_M) - E_{pv}^{el}(q_P) \quad (4)$$

where q stands for the reaction coordinate along the IRC path, and thus, $\Delta_{pv}E_{el}(q_e)/(hc) = 1.61 \times 10^{-12}\text{ cm}^{-1}$. The ground state value $\Delta_{pv}E_0$ would have to be calculated by the expectation value of $\Delta_{pv}E_{el}(q)$ for the multidimensional vibrational ground state wave function. This would change the result somewhat, but not fundamentally.^[27] An approximate correction to provide $\Delta_{pv}E_0$ is about 20% (see SI). The maximum difference $\Delta_{pv}E_{el}(q_{\max=25})$ or $\Delta_{pv}E_{el}(q_{\max=145})$ is about $8.2 \times 10^{-12}\text{ cm}^{-1}$.

We carried out tunneling calculations using the quasi-adiabatic channel reaction path Hamiltonian approach of Ref. [26]. To estimate the validity of this approximation, we also did a two-dimensional torsional treatment using the $V(\tau_1, \tau_2)$ potential employing the GENIUSH program package,^[28] without zero point energy correction. The more accurate reaction surface Hamiltonian approach^[29] is not expected to change these results by orders of magnitude given the related small correction in the 1D quasi-adiabatic channel results.

Since the ΔE_{\pm} tunneling splittings are very small because of the high barriers and complex tunneling paths, their direct variational computation is not easily possible due to numerical limitations. To estimate the ground-state tunneling splitting, we invoked an extrapolation technique that has been described elsewhere and is based on the WKB theory, but combined with “numerically exact” results for large tunneling splittings (see Ref. [14] for details). The results for tunneling splittings from the various approximate calculations are summarized in Table 1, including calculations involving two further IRC

Table 1. Estimated tunneling splittings for different 1D and 2D computational models (see text for more information). For the different 1D models, both Born–Oppenheimer (BO) and lowest quasi-adiabatic channel (AC) results are given.

Model	$\Delta E_{\pm}(\text{BO})/hc [10^{-24}\text{ cm}^{-1}]$	$\Delta E_{\pm}(\text{AC})/hc [10^{-24}\text{ cm}^{-1}]$
1D flip-flop	1.3	1.1
1D IRC	0.8	1.7
1D IRC(b)	0.03	0.1
1D IRC(ab)	0.2	0.6
2D	33	–

paths containing only the (b) or both (a) and (b) transition structures. This provides an estimate for the contribution of the less favorable tunneling path (b) to contribute little compared to (a), whereas the extension to a 2D treatment provides a larger change by an order of magnitude, which is in part due to the neglect of zero point energy in the 2D calculation. Extension to an exact 9D treatment is difficult but is not expected to change the order of magnitude, as the 2D treatment includes the main motions and this allows for an estimate of the possible changes.

2D energy levels were obtained as well with the GENIUSH program package. Delocalization of wave functions corresponding to tunneling switching starts at about 2000 cm^{-1} . Besides the parent isotopomer, we also obtained computational results for HSSSD and HSS^{34}SH . Tunneling splittings of the vibrational ground state (obtained with the 2D variational treatment) are estimated to be $4.6 \times 10^{-28}\text{ cm}^{-1}$ (HSSSD) and $2.9 \times 10^{-23}\text{ cm}^{-1}$ (HSS^{34}SH).

Our main finding is that the tunneling splitting ΔE_{\pm} in the vibrational ground state is substantially smaller than the parity-violating energy difference [Eq. (5)]:

$$\Delta E_{\pm}/(hc) \approx 10^{-23}\text{ cm}^{-1} \ll \Delta_{\text{pv}}E/(hc) \approx 10^{-12}\text{ cm}^{-1} \quad (5)$$

Thus, parity violation dominates the quantum dynamics in the ground state of this molecule. The small values ΔE_{\pm} are in line with the fact that no splittings due to tunneling were observed by spectroscopic studies. While the results of $\Delta_{\text{pv}}E$ and tunneling are approximate, the large difference of many orders of magnitude guarantees that our conclusion on the dominance of parity violation in this chiral molecule is firm. It is thus safe to conclude that trisulfane is an appropriate molecule for experiments on molecular parity violation from this point of view. Its modest complexity with only three non-hydrogen atoms and the modest barriers for stereomutation make it accessible to the infrared route for such experiments (see Figure 1 and Refs. [9, 12, 13, 16]). The S-H infrared chromophore near 2500 cm^{-1} , well above the barrier, makes states with large parity splittings accessible energetically. The relatively high vibrational density of states of about 10 states per cm^{-1} in this energy range favors intramolecular coupling to the low-frequency modes. Thus, it is likely that some accessible states would actually show sufficiently large parity splittings and are not governed by the small splittings arising with decoupling of the high frequency modes, and slow quasi-adiabatic above barrier tunneling. While the high density of states practically guarantees that sufficiently strong rovibrational couplings will make tunneling sublevels of well-defined parity accessible via the S-H infrared chromophore, for example, their spectroscopic assignment could represent an appreciable challenge. Ultimately, accurate full dimensional rovibrational variational calculations (for low angular momentum quantum numbers J) are possible today for molecules with up to five atoms at modest energies.^[28] Such calculations, in conjunction with high-resolution spectra available by current techniques in our laboratory,^[13, 30] will make such a definitive assignment possible. The shape of the parity-violating potential shows a relative, but not absolute maximum of the magnitude of E_{pv} near the equilibrium geometry of the chiral *trans*-like isomer. While larger values of $\Delta_{\text{pv}}E$ would be desirable, the magnitude should be sufficient for detection with the experimental setup of Ref. [13]. As with many other examples, one finds vanishing E_{pv} also at some chiral geometries, an effect discussed and explained repeatedly before for other molecules.^[7] The maximum of E_{pv} as a function of the torsional angle is in the range expected for a molecule with several sulfur atoms. Finally, the isotopomer HSS^{34}SH shows isotopic chirality with a $\Delta_{\text{pv}}E$ of (hc)

10^{-13} cm^{-1} in the *cis* geometry, about an order of magnitude lower than the *trans*-like isomer and in line with findings for isotopic chirality in $\text{PF}^{35}\text{Cl}^{37}\text{Cl}$.^[25] Thus, we can summarize that the *trans*-like isomer of HSSSH is by all requirements an almost ideal molecule for measuring the parity-violating energy difference $\Delta_{\text{pv}}E$ in the relatively near future, even if the experiment remains difficult.

Trisulfane is also the first example where the interesting tunneling dynamics with a double rotor has been studied in conjunction with parity violation. It turns out in this case, however, that a one-dimensional approximation with sequential rotation of each rotor is a reasonable approximation. On the other hand, with only five atoms, HSSSH is also becoming amenable to full nine-dimensional vibrational variational calculations in the near future. This opens interesting possibilities of extracting fundamental parameters of the Standard Model of Particle Physics by combining accurate calculations with accurate experimental results, once available. Thus, theory and high-resolution spectroscopy of chiral molecules have the potential to contribute to fundamental physics more commonly investigated at high-energy accelerators.

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Keywords: ab initio calculations • chirality • molecular parity violation • trisulfane • tunneling

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