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High-resolution FTIR spectroscopy of trisulfane HSSSH: a candidate for detecting parity violation in chiral molecules†

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We report the first successful high-resolution analyses of the Fourier transform infrared (FTIR) spectrum of trisulfane. A band centered at 861.0292 cm^{-1} can be assigned unambiguously to the chiral *trans* conformer by means of ground state combination differences in comparison with known rotational spectra. A second band near 864.698 cm^{-1} is tentatively assigned to the *cis* conformer by comparison with theory. The results are discussed in relation to their importance for experimental attempts to measure the parity violating energy difference $\Delta_{pv}E$ between the ground states of enantiomers of chiral molecules.

Introduction

According to traditional quantum chemistry involving only the electromagnetic force the ground state energies of the enantiomers of chiral molecules as well as the energies of equivalent excited quantum states are exactly identical by symmetry. When the parity violating weak "nuclear" force causing beta-decay[1–8] is included in the "electroweak quantum chemistry" (see ref. 9–14 and references cited therein), one predicts an energy difference $\Delta_{pv}E_0$ between the ground states of enantiomers and a corresponding reaction enthalpy $\Delta_{pv}H_0^{\ominus}$ for the stereomutation reaction converting P and M enantiomers in the case of axially chiral molecules:

$$\mathrm{P} \rightleftharpoons \mathrm{M} \quad \Delta_{pv}H_0^{\ominus} = E_0(M) - E_0(P) = N_A\Delta_{pv}E_0 \qquad (1)$$

While there has been a considerable body of theoretical work on this topic recently (reviewed in ref. 13–16), the experimental determination of $\Delta_{pv}E_0$, which is possible, in principle, following a scheme proposed three decades ago,[17] has remained a challenge which has not been met with success so far (see ref. 18 and also reviews[19,20] for various attempts to detect parity violation in chiral molecules including also other approaches). Recent experimental tests have indicated that values of $\Delta_{pv}E_0$ as small as about 100 aeV should be detectable with an existing experimental set-up.[21] An important step in the preparation for such experiments is the selection of a suitable molecule for such experiments. It should satisfy the following conditions:[18,19,22] (i) the tunneling splitting in the ground state $\Delta E_{\pm}$ must be small compared to $\Delta_{pv}E$, (ii) a high resolution analysis of infrared or visible/UV spectra must be possible, (iii) molecular states of well-defined parity must be reachable either from laser excitation near or above the barrier for interconversion in the electronic ground state or by excitation to an achiral (planar) excited electronic state. According to a recent theoretical and spectroscopic study, 1,2-dithiine ($C_4H_4S_2$) is a suitable candidate for such experiments, in principle, having, however, the drawback of a relatively large number of atoms and a corresponding spectroscopic complexity.[18,22] Another suitable molecule with fewer atoms has been identified in recent theoretical calculations,[23] HS_3H, for which, however, so far no high resolution spectroscopic analysis in the optical region (infrared or Vis/UV) has been achieved. The present communication reports the first such high resolution analysis of infrared spectra for this molecule.

Polysulfanes HS_nH have been prepared and studied by low resolution spectroscopy very long ago (see ref. 24–27 and references therein). Trisulfane, HS_3H, in particular, has also been identified by high resolution pure rotational spectroscopy.[28–33] It has three low energy conformers, the two enantiomers of the chiral *trans* structure (P and M in current nomenclature[23]) with C_2-symmetric equilibrium geometry and an achiral *cis* structure with C_s point group symmetry (see Fig. 1). These conformers have rather similar ground state energies and can be interconverted along a reaction path including the *cis* and *trans* conformers with a barrier of a little more than 2000 cm^{-1}. The ground state tunneling splitting $\Delta E_{\pm}$ is less than (hc) 10^{-20} cm^{-1}, which is much less than the predicted parity violating energy difference $\Delta_{pv}E_0 = (hc) \times 10^{-12}$ cm^{-1}. As discussed in detail in ref. 23, the tunneling splittings from calculations with the quasiadiabatic channel reaction path Hamiltonian approach and from calculations on a two dimensional potential surface including both -SSH rotors differ somewhat. However, the uncertainties from these approximations or from

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† Electronic supplementary information (ESI) available: Linelists of transitions assigned are included. See DOI: 10.1039/c7cp01139c

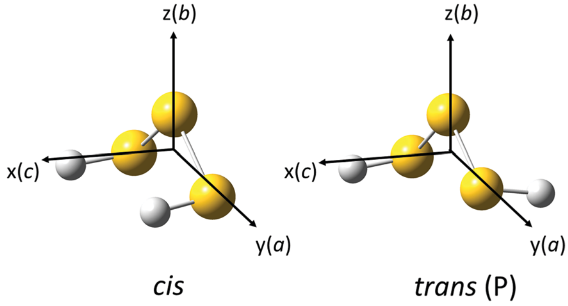

Fig. 1 Structures of the *trans* and *cis* conformers of HSSSH with their principal axes *a*, *b*, *c* and axes definition. The C_2 axis in *trans*-HSSSH coincides with the *z* axis which is retained as the C_2 axis for the heavy atom SSS plane for both conformers.

the *ab initio* calculations of the barriers do not affect the conclusion that $\Delta E_{\pm}$ is by many orders of magnitude smaller than $\Delta_{\mathrm{pv}}E$. Thus trisulfane is certainly adequate for experiments from this point of view. While the two coupled S–S–H internal rotors lead to some complexity, this is compensated to some extent by the small number of atoms, noting that four to five (at most six) atomic systems are the current limit in size for full dimensional quantum mechanical vibrational–rotational–tunneling treatments.[34–36] As the barrier of about 2000 cm^{-1} indicates, tunneling sublevels of well-defined parity are energetically accessible to current high resolution infrared laser technology.[21] Thus an exploratory high resolution analysis of the infrared spectra of HSSSH seemed promising. Trisulfane has also recently been discussed as a candidate for "missing sulfur" in dense interstellar clouds and circumstellar regions.[37]

Experimental

Trisulfane was prepared following ref. 38 by reaction of H_2S with bromine at −78 °C following a formal stoichiometry:

$$3H_2S + 2Br_2 = HS_3H + 4HBr$$

Elemental bromine was added dropwise to a cooled saturated solution of HCl in liquid H_2S at −78 °C. A vigorous reaction occurred. Stirring was continued for 16 h at −78 °C. After evaporation of H_2S and HCl used in excess, the remaining yellow liquid was characterised *via* NMR spectroscopy where the broad singlet with a shift of 4.1 ppm corresponds to the protons of H_2S_3. The purity was roughly 80%, the main impurity being H_2S_4 with a much lower vapour pressure. NMR spectra were measured in $CDCl_3$ as solvent. The identity of the gaseous sample was also obvious from the line resolved infrared spectrum allowing for the determination of the known ground state rotational parameters (see below).

The rovibrational spectrum of HSSSH was recorded between 800 and 930 cm^{-1} using the Fourier transform infrared (FTIR) spectrometer Bruker IFS 125 HR Zürich Prototype (ZP) 2001, which has been described elsewhere.[39–42] The instrument-limited unapodized resolution is 0.0008 cm^{-1} with the Doppler width of HSSSH being about 0.001 cm^{-1} at 860 cm^{-1} and 296 K.

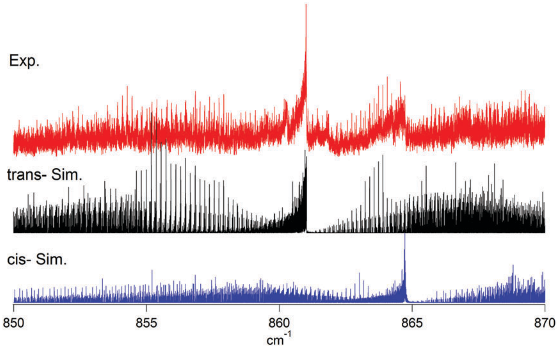

Fig. 2 An overview of the asymmetric SSH bending fundamental of HSSSH between 845 and 870 cm^{-1}. Upper part: Experimental spectrum. Middle part: Simulated spectrum of *trans*-HSSSH based on parameters reported in Table 1; lower part: simulated spectrum of *cis*-HSSSH based on a tentative assignment. The experimental conditions are: P = 1.4 mbar; l = 3 m, decadic absorbance $\lg(I_0/I)$ is shown with the maximum in the experimental spectrum corresponding to $\lg(I_0/I)_{\max}$ = 0.16. The simulation of *trans* and *cis* spectra uses similar values for the *a*-type transition intensities.

The pressure of the gaseous sample was maintained at 1.4 mbar in order to optimise the signal-to-noise ratio while preventing substantial pressure broadening. The linewidth of a typical unblended transition at 860 cm^{-1} is about 0.001 cm^{-1}, indicating Doppler limited resolution in this spectral region. Fig. 2 shows an overview spectrum of the SSH bending mode, from which two *a*-type band centers are visible. By initial inspection of the Q-branch heads in rotationally resolved spectra and comparison to previously calculated fundamental wavenumbers,[23] a tentative assignment can be made to the *trans* (861.03 cm^{-1}) and *cis* (864.70 cm^{-1}) conformers.

Results of the analysis

To start with the detailed analysis of the rovibrational spectra, a simulated spectrum was generated based on the estimated band center by inspecting the high resolution data and previously reported ground state spectroscopic constants determined from the pure rotational spectra.[33] As can be seen in Fig. 2, a series of strong absorption features which are relatively broad (FWHM = 0.003 cm^{-1}, about three times the Doppler width in this range) is clearly visible, which can be considered as clusters of neighbouring transitions. A comparison between the experimental and simulated spectra indicates that such clusters are transitions sharing common K_a but differing in J values using conventional notation (J, K_a, K_c) for the asymmetric top levels.[43] Due to this extremely close proximity of adjacent transitions and the noisy background in the spectrum, Loomis–Wood diagrams[43–45] were constructed to display regularly recurring patterns in an effort to locate a spectral region in which such neighbouring transitions are relatively spread out (towards higher J values, away from the band center) while their intensities are still sufficient to be assigned. To ensure the unambiguous assignment, ground state combination differences (GSCDs) were calculated using pairs of assigned transitions in the P and R branches sharing a common upper state and checked with ground state data from previously reported pure rotational spectra.[33] Assigned transitions were fitted using Watson's *A*-reduced effective Hamiltonian[46] in the I^r representation within the WANG program.[43,47] Subsequently, the simulated spectrum was refined, leading to the assignment of more transitions. All ground state parameters including the rotational constants *A*, *B*, *C* and the centrifugal distortion constants Δ_J, Δ_K and Δ_{JK} were held fixed during the fitting procedure to the values reported in previous studies of pure rotational spectra.

The spectra exhibit two Q branches as can be seen in Fig. 2. The preliminary assignment then focused on the clusters of the stronger band centered at 861.03 cm^{-1}, which are visible as "spikes" in the overview spectrum in Fig. 2. Following the procedure described above, the assigned *R* and *P*-branch pairs sharing a common upper state were found to match the GSCDs based on previously reported pure rotational spectra of the *trans* conformer. As the observed spectrum is noisy, the assignment was limited to the strongest lines on purpose to avoid possible misassignment. In total, 287 *a*-type (*oo* ↔ *oe* and *ee* ↔ *eo*) transitions were assigned to the *trans*-HSSSH isomer with $J_{\max}$ = 29 and $K_{c\,\max}$ = 29. The resulting spectroscopic constants are summarized in Table 1. Additionally, 110 GSCDs were calculated from assigned transitions and fitted separately and the resulting rotational parameters are presented in Table 2.

Our rovibrational analysis shows that the assigned *a*-type band centered at 861.029170(84) cm^{-1} corresponds to the *trans*-HSSSH, based on the GSCDs and the fact that all lower state constants were held fixed in the fit to the MW data reported for this conformer, and yet the root-mean-square deviation d_{rms} is only 0.000158 cm^{-1}. Fig. 3 shows a comparison of a measured section of the *P*-branch with a simulation based on the values reported in Table 1. The effect of nuclear spin statistics (3 : 1) is included in the simulation, although it is not very pronounced in the experiment because of the noise level. As can be seen, the agreement between experiment and simulation is good for the strong lines despite the high noise levels. In addition, 110 GSCDs were calculated from assigned transitions and fitted separately and the resulting rotational constants are presented in Table 2.

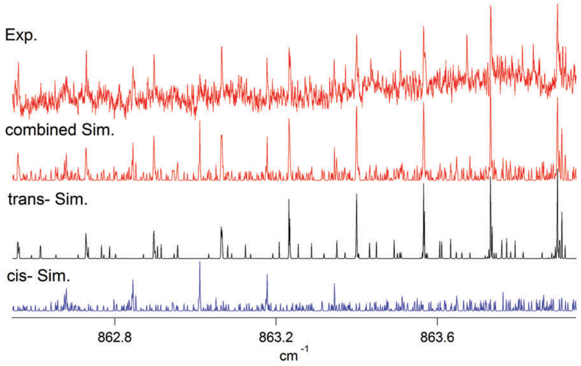

Fig. 3 An overlapping section of the *P*-branch of the *cis* conformer and *R* branch of the *trans* conformer of the asymmetric SSH bending fundamental of HSSSH. Upper part: The experimental spectrum is shown. Middle upper part: Simulated spectrum of both *trans* and *cis* conformers. Middle lower part: Simulated spectrum of the *trans*-HSSSH based on a tentative assignment. Lower part: Simulated spectrum of the *cis*-HSSSH. Conditions see Fig. 2, lg(I_0/I)$_{\max}$ = 0.08.

Table 1 Spectroscopic constants in cm^{-1} for the ground state and the asymmetric SSH bending fundamental of *trans*-HSSSH (uncertainties are given in parentheses in terms of the last stated digits as 1σ)

	v = 0 (GSCD)	v = 0[33]	v = 1
$\tilde{\nu}_0$/cm^{-1}	0	0	861.029170(84)
A/cm^{-1}	0.47100(84)	0.47028867	0.4703469(18)
B/cm^{-1}	0.0917370(72)	0.09173522	0.09202751(76)
C/cm^{-1}	0.0791070(68)	0.07911129	0.07849384(81)
Δ_J/10^{-6} cm^{-1}	0.0340(10)	0.035020	0.08860(49)
Δ_K/10^{-6} cm^{-1}	4.2381[a]	4.2381	5.2293(77)
Δ_{JK}/10^{-6} cm^{-1}	−0.39040	−0.39040	−0.3934(32)
d_{rms}/cm^{-1}	0.000232		0.000158
N_{data}	110	117	287

[a] Values without parenthesis were held fixed to the corresponding values of the ground state obtained by the previous MW study.[33]

Most of the values $\Delta_{\text{OC}} = \tilde{\nu}_{\text{obs}} - \tilde{\nu}_{\text{calc}}$ for the GSCD fit are below 0.0005 cm^{-1} with d_{rms} = 0.000232 cm^{-1}. Considering that Δ_{OC} for the GSCD is typically twice the value of those of the rovibrational fit (generally below 0.0005 cm^{-1} in this case) arising from propagation of errors and the fact that centrifugal distortion constants Δ_J, Δ_K and Δ_{JK} were all held fixed to the previously reported MW work, such a small d_{rms} is yet another demonstration of the accuracy of the assignment. When comparing the resulting ground state rotational constants with the MW values of both conformers, *B* and *C* are sufficiently accurate to allow for a conclusive assignment of the *trans* conformer. *A* has a relatively large uncertainty that falls within the uncertainties of *A* for both conformers because the assigned transitions are of *a*-type. We can conclude with confidence that this band can be assigned to the asymmetric -SSH bending fundamental of *trans*-HSSSH.

Despite the low intensity of the band centered at 864.70 cm^{-1}, which is roughly a third of that of the band discussed above, an effort was made towards an assignment. A second simulated spectrum was made based on the previously reported MW spectroscopic constants of *cis*-HSSSH for the ground state with this new band center. Tentative assignments were made on a trial-and-error basis so that the resulting simulation reproduces the experimental spectrum best. A satisfactory simulation based

Table 2 Comparison of ground state rotational constants of HSSSH in MHz

	This study (GSCD)	*trans* MW[a]	*trans*[b]	*cis* MW[a]	*cis*[b]
A/MHz	14 120 (25)	14098.89950 (30)	13 802	14103.20771 (17)	13 796
B/MHz	2750.15 (22)	2750.15267 (16)	2734	2752.759027 (81)	2737
C/MHz	2371.57 (20)	2371.69686 (86)	2347	2373.869384 (86)	2350

[a] Ref. 33. [b] Theory, MP2/cc-pVTZ, ref. 23.

Table 3 Spectroscopic constants in cm^{-1} for the ground state and the asymmetric SSH bending fundamental of *cis*-HSSSH

	v = 0[33]	v = 1
$\tilde{\nu}_0$/cm^{-1}	0	864.6985(15)
A/cm^{-1}	0.47043235[a]	0.47080(7)
B/cm^{-1}	0.09182216	0.093540(5)
C/cm^{-1}	0.07918375	0.07918(6)
Δ_J/10^{-6} cm^{-1}	0.0351	0.28(18)
Δ_K/10^{-6} cm^{-1}	4.2163	4.7(11)
Δ_{JK}/10^{-6} cm^{-1}	−0.38957	0.33(81)
d_{rms}/cm^{-1}	0.0004	
N_{data}	72	29

[a] Values without parenthesis were held fixed to the corresponding values of the ground state obtained by the previous MW study[33] (see also Table 1).

on such a tentative assignment is shown in Fig. 3 and the spectroscopic parameters are given in Table 3. The series of transitions of considerable intensity aside from the *trans* clusters in Fig. 3 can be identified and both series are visible in the Loomis–Wood diagram. The Q-branch head can also be reproduced well as shown in Fig. 2. However, the inferior signal-to-noise ratio prevented the assignment from being carried out in the same way as for the *trans* conformer. Some spectral features fail to align with the simulation, possible explanations being (1): the signal-to-noise ratio for the *cis* conformer is at the border line level for assignment so that transitions likely are well mixed with the noise; (2) as a result, this tentative assignment containing a few transitions can only account for a limited coverage of quantum numbers; (3) there can be interactions with other levels, notably the symmetric SSH bending fundamental which is predicted only ∼10 cm^{-1} away. When comparing the two experimental band centers (861.029170(84) cm^{-1} for the *trans* and 864.6985(15) cm^{-1} for the *cis* conformer, ∼3.5 cm^{-1} apart) of the asymmetric SSH bending mode to the calculated anharmonic wavenumbers $\tilde{\nu}$ at MP2/cc-pVTZ level (860.5 cm^{-1} for the *trans* and 864.8 cm^{-1} for the *cis* conformer, ∼4.2 cm^{-1} apart),[23] the agreement within less than 1 cm^{-1} in the shift between the *cis*- and *trans*-HSSSH is excellent. Furthermore, the calculated IR transition moment μ_a for a-type transitions in the *trans* and *cis* conformers are about the same, whereas the total IR intensity is predicted to be larger by a factor of 1.4 for the *trans* conformer.[23] The intensity difference is visible in the overview spectrum in Fig. 2. One could attempt to obtain more information about this transition by searching for the theoretically predicted c-type transitions with enhanced sensitivity. Fig. 4 shows also a section of the P branch of the bending fundamental of HSSSH.

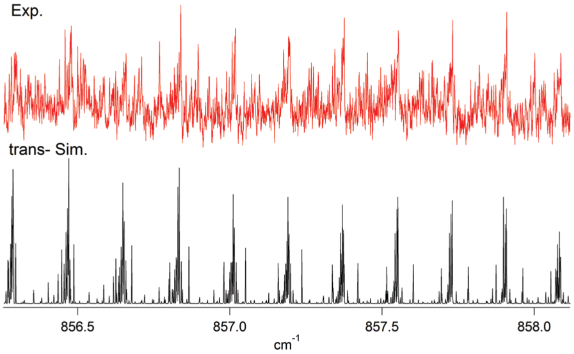

Fig. 4 A detailed section of the P branch of the *trans* conformer of the asymmetric SSH bending fundamental of HSSSH. Upper part: The experimental spectrum recorded at 1.4 mbar is shown at the top. Lower part: Simulated spectrum of the *trans*-HSSSH. Conditions see Fig. 2, $\lg(I_0/I)_{\max}$ = 0.075.

Table 4 Vibrational fundamental wavenumbers (in cm^{-1}) and intensities (in parentheses in km mol^{-1}) from *ab initio* calculations[a] and experiment

	cis[a]	*trans*[a]	(Exp.)[b]
ν_1 (A/A')	2616.1 (0.84)	2622.5 (0.11)	2540
ν_2 (A/A')	874.1 (3.5)	871.6 (0.03)	868
ν_3 (A/A')	502.8 (0.40)	502.0 (0.36)	487
ν_4 (A/A')	325.2 (15.7)	300.3 (20.5)	320
ν_5 (A/A')	206.9 (0.05)	206.0 (0.003)	211
ν_6 (B/A'')	2619.5 (0.06)	2621.7 (0.04)	2532
ν_7 (B/A'')	864.8 (5.9)	860.6 (8.5)	861.03[c]
ν_8 (B/A'')	497.6 (23.4)	496.7 (21.5)	477
ν_9 (B/A'')	309.1 (9.3)	324.7 (15.7)	320

[a] This work, anharmonic fundamental wavenumbers (MP2/cc-pvTZ) and intensities in the double harmonic approximation. The symmetry labels A, B, refer to the C_2 point group of *trans* and A', A'', to the C_s point group of *cis*. [b] Approximate results from solution spectra with no clear distinction of *cis* and *trans* isomers ref. 25 and 27. [c] This work, gas phase value for *trans*, the value for *cis* is 864.7, see Tables 1 and 3.

Our unambiguous assignment of a vibrational fundamental in the gas phase spectrum can also serve as benchmark in comparison with theoretical calculations.[23,32,37] Table 4 provides a summary of theoretical and experimental values for the vibrational fundamentals of trisulfane. Previous experimental results were obtained from low resolution spectra in solution without clear assignment to the *cis*- or *trans*-isomers,[25] whereas low resolution estimates of three gas phase band centers were assigned to antisymmetric modes of the trans isomer (2542, 860, 480 cm^{-1}), but without rotational analysis or proof of the assignment.[31] Our definitive value for ν_7 at 861.03 cm^{-1} is in surprisingly good agreement with our theoretical value for this fundamental in Table 4. While no such good agreement is expected and found for some of the other fundamentals, we note that the recent prediction for ν_7 in ref. 37 (829.2 cm^{-1}) is much too low, presumably because of an overcorrection of the density functional theoretical results (with the B3LYP functional in the Gaussian package), with a scaling factor 0.9687 used in ref. 37. Thus the predictions of ref. 37 should be considered with some reservation in the context of assigning vibrational spectra in astrophysical observations. The theoretical intensities in Table 4 should be considered to be rough estimates only, given the double harmonic approximation used.

However, the prediction of strong bands in the far infrared range indicates their accessibility to high resolution analyses and such work is planned, using our ideal existing setup at the infrared beamline at the Swiss Light Source.[22]

Discussion and conclusions

Using essentially Doppler limited high-resolution FTIR spectroscopy of the trisulfane (HSSSH) fundamental near 860 cm^{-1}, we have been able to unambiguously assign the band centered at

861.029 cm^{-1} to the chiral *trans* conformer by means of 110 accurate infrared ground state combination differences in comparison with very precise existing microwave results from ref. 33. A total of 287 assigned transitions in this band lead to accurate rotational parameters for the excited vibrational state which can be used as a starting point for further analysis. Also the band centered at 864.698 cm^{-1} can be assigned with good confidence to the achiral *cis* conformer by means of comparison with theory,[23] even through the experimental information is more limited. These first high resolution analyses of the infrared spectra of trisulfane open the path towards further analyses with the aim of identifying states which are suitable for the experimental approach[17,21] towards measuring the parity violating energy difference $\Delta_{\text{pv}}E$ between the P and M enantiomers of the *trans* isomer of this chiral molecule.

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