ab initio Calculation of ^{33}S Quadrupole Coupling Constants. Reanalysis of the ^{33}S Hyperfine Structure in the Rotational Spectrum of Thiirane

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We present quantum chemical calculations on the MP4(SDQ) level with basis sets of high local quality to determine the nuclear quadrupole coupling tensor of ^{33}S in a series of molecules, which were investigated up to now by microwave spectroscopy. The analysis of the nuclear quadrupole coupling in the rotational spectra provided experimental information on the tensors. As an example for such an analysis, improved values for thiirane, $C_2H_4{}^{33}S$, are given: $\chi_{aa} = -32.9425(78)$ MHz, $\chi_{bb} = -16.402(14)$ MHz, $\chi_{cc} = 49.345(14)$ MHz.

Introduction

Since the advent of microwave spectroscopy after 1945 one property, which could be observed, is the hyperfine structure (hfs) of rotational transitions produced by the interaction of molecular and nuclear rotation via the electric nuclear quadrupole moment and the molecular field gradient tensor at the site of the nucleus. The information provided by the analysis of the hfs is the electric field gradient (efg) tensor in the $g = a, b, c$ principal inertia axis system with the tensor elements $\partial^2 V/\partial g\, \partial g' = q_{gg'}$, $g, g' = a, b, c$ (V electric potential). This tensor reflects the bonding situation of an atom with a nucleus having a nuclear spin $I \geq 1$ and a nuclear quadrupole moment. The nucleus acts as a probe for the efg tensor at its coordinates.

The technique of analysis of the hfs is described in many publications e.g. [1]. The use of the electric field gradient tensor elements $q_{gg'}$ or the nuclear quadrupole coupling tensor elements $\chi_{gg'} = e\,Q\,q_{gg'}$ (e electron charge, Q nuclear quadrupole moment) to characterize chemical bonds is discussed in detail e.g. in [2].

In the last decades the hfs of many nuclei was investigated and evaluated, e.g. ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, I, ^{17}O, ^{14}N, ^{11}B, ^{10}B, and D. Until recently only few molecules could be worked on containing ^{33}S, as the natural abundance is only 0.76% and a preparation is sometimes difficult and always expensive.

The sensitivity, resolution, and accuracy obtained by molecular beam Fourier transform microwave spectroscopy [3] allowed us to investigate the hfs of ^{33}S containing molecules in natural abundance. This opens an interesting and wide field, as sulfur exists in different bond situations.

As quantum chemistry advanced tremendously, it is interesting to compare the experimental determination and calculation of the efg tensor elements $q_{gg'}$. These calculations provide the complete tensor with diagonal and off-diagonal elements referred to the principal intertia axis system $g = a, b, c$, whereas the analysis of the experiments results only in exceptional cases in a complete tensor. The usual result is the set of diagonal elements q_{gg} or χ_{gg}. Sometimes symmetry forces some off-diagonal elements to become zero or considerations using isotopomers with a rotated principal inertia axis system allow the determination of the off-diagonal tensor elements [4] from the rotational spectra.

It should be mentioned that experiments and quantum theory determine a slightly different quantity: The efg tensor of a molceule in the vibrational ground state and the efg tensor of a molecule with a certain fixed structure, respectively.

First, we present ab initio calculations for molecules performed in Basel. Second, as an example of an analysis of ^{33}S-hfs, results for thiirane will be given. The spectra were remeasured in Kiel and Aachen to improve former results [5].

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Quantum Chemical Methods

All calculations were performed at experimental microwave gas phase structures, usually r_s-structures, in a few cases r_0-structures [6]. The calculations are for the rigid structure, i.e. vibrations are neglected. We expect the error due to this approximation to be a few percent (see also discussion below). Hence, high accuracy of the structure is of minor importance. Møller-Plesset perturbation theory was applied on the MP4 (SDQ) full level using the Gaussian 94 [7] set of programs. Basis sets of high local quality, which had been applied successfully in the calculation of deuterium- [8–10], lithium- [11], nitrogen- [12, 13] and oxygen- [14] quadrupole couplings were used (note that Chesnut and Moore [15] have recently used the same concept under the name "locally dense basis sets" for the calculation of chemical shifts).

Using a quite large basis set on the sulfur yielded results very close to experiment, in contrast to previous calculations of other chemical elements. Hence, we did not use the nuclear quadrupole moment of ^{33}S as a fit parameter but applied the IUPAC value of $-67.8 \cdot 10^{-31}\,\mathrm{m}^2$ [16]. Therefore, the results in this paper were obtained fully ab initio (at the experimental structures).

We performed a few calculations on H_2S, H_2CS and HNCS with distorted geometries to study the influence of the structure on the size of the quadrupole coupling constants χ. A change of 1% in the valence angle results in about 0.5% change in the couplings. A change of 1% in the S-X bond-length(s) yields a change of about 2% in the coupling with the exception of HNCS, where the change is about 6% for the large components of the coupling tensor, but about 15%, i.e. 1 MHz, for the smallest component. In general, the structures used here are more accurate than 1%, hence the error due to the inaccuracy of the structures should be negligible. However, in extreme cases, if only an r_0-structure is available and the coupling is very sensitive (as in HNCS), such an error might be the origin of a deviation from experiment. With the above test calculations we estimated the vibrational contributions to the quadrupole coupling constants to be of the order of a few percent (probably typically 2 to 3%).

A further test was performed to estimate the intramolecular basis set superposition error of the efg. For H_2CS this error turned out to be about 0.2%. This is negligible compared to the other inaccuracies.

Basis Set Evaluation

Whereas for molecular properties balanced basis sets are appropriate, the calculation of local properties (e.g. the efg at a nucleus) can be performed much more efficiently with basis sets which have locally a very high quality, whereas atoms further away are treated with smaller basis sets. Here we use an extremely large basis on sulfur, medium sized basis sets on the nearest (basis A) or nearest and next nearest neighbours (basis B), and a small basis on all atoms further away.

The sulfur basis was constructed starting with a primitive regularised even-tempered basis set [17] for the occupied orbitals. For H_2S and H_2CS the size was increased until the change of the electric field gradient was negligible (here and in the following we call a change or an error negligible, if it is small compared to the expected error due to the neglected vibrations, which we estimate to be a few percent). The resulting basis consisting of 20 s- and 15 p-functions was contracted to 12 s- and 9 p-functions such that the change again was negligible. With the same citeria, d-functions and then f-functions were added to make the electric field gradient converge on the MP4(SDQ) level in these two molecules. The final basis is given in Table 1 and was used in all further calculations.

The medium sized basis set on the hydrogens consisted of Dunning's (4s)/[2s] basis [18] scaled by 1.2 and enlarged by a set of p-functions with exponent 1.2. For the first row elements, Dunning's (9s 5p)/[4s 2p] basis [18] was enlarged by two sets of d-functions (exponents 1.6 and 0.4 for C, 1.8 and 0.45 for N, 2.0 and 0.5 for O, and 2.2 and 0.55 for F). For the second row elements, the (12s 9p)/[6s 5p] basis by McLean and Chandler [19] was supplemented with two sets of d-functions (exponents 0.88 and 0.22 for P, and 1.0 and 0.25 for S). For the direct neighbours of S, always the medium sized basis was used. In basis B, the medium basis was also used for atoms other than hydrogens if they were one step further away. We expected to improve the results mainly for conjugated systems like thiophene with basis B. On Ge we used the (14s 12p 6d 1f)/[8s 7p 3d 1f] basis set by Curtiss et al. [20, 21].

The small basis used for hydrogen was Dunning's (4s)/[2s] basis [18] scaled by a factor of 1.2, whereas for first row atoms the (7s 3p)/[4s 2p] basis by Roos and Siegbahn [22] was applied.

Table 1. Basis set evaluated for sulfur (different contractions are subdivided by underlining).

s-Functions		*p*-Functions	
Exponent	Coefficient	Exponent	Coefficient
720 957.780017	0.00002	3 734.353241	0.00007
316 938.445246	0.00001	1 709.715820	0.00013
139 328.516675	0.00009	782.766920	0.00070
61 249.860501	0.00017	358.377716	0.00241
26 925.897878	0.00055	164.077689	0.00898
11 836.826575	0.00145	75.120430	0.02969
5 203.557705	0.00409	34.392726	0.08863
2 287.522979	0.01122	15.746177	0.20884
1 005.612252	0.03014	7.209143	1.
442.074685	1.	3.300595	1.
194.339346	1.	1.511126	1.
85.433033	1.	0.691846	1.
37.557002	1.	0.316751	1.
16.510340	1.	0.145019	1.
7.258069	1.	0.066395	1.
3.190702	1.		
1.402656	1.		
0.616618	1.		
0.271070	1.		
0.119164	1.		

f-functions	
Exponent	Coefficient
0.868655	1.
0.335	1.

d-functions	
Exponent	Coefficient
3.1519449	1.
1.2592668	1.
0.503103	1.
0.201	1.

Results and Discussion of the Quantum Chemical Calculations

In Table 2 the results of all calculations are collected and compared with the experimental couplings. Where basis A and B are identical, the values are tabulated under B. Also given are values by Palmer [23], calculated including electron correlation by complete active space scf studies. The improvement by the present calculations is shown by the rms deviations between experiment and calculation. The rms value of 0.96 MHz corresponds to 2 to 3% relative to the largest component, or 1% of the whole range of couplings, which is probably very close to the error due to the neglect of the zero point vibrations. Figure 1 shows the calculated (basis B) versus the experimental values.

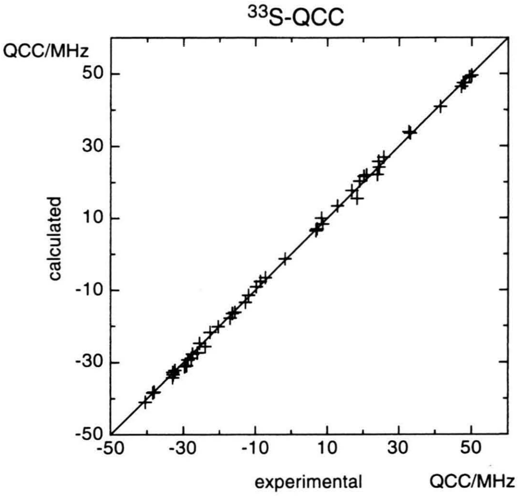

Fig. 1. ab initio calculated (basis B) versus experimental ^{33}S-quadrupole coupling constants for the compounds in Table 2. The dimers are not included. Where available, all diagonal terms were used; in the case of CH_3SSCH_3 the off-diagonal terms are included. The line has slope one, i.e. it is not a fitted line.

Basis B was mainly introduced to improve results for conjugated systems, where atoms which are not neighbouring the sulfur atom are part of the π-system. For the 30 coupling elements where basis A and B are different, the rms deviation between experimental and calculated couplings was reduced from 1.41 MHz for basis A to 1.09 MHz for basis B. However, a detailed analysis shows that the largest improvements are for isothiazole, thiophene, thiazole, OCS and HNCS, whereas, e.g., the substituted thiiranes show only a minor improvement. This is exactly what we expected, and it shows that for π-systems the basis has to be of reasonably good quality throughout the π-system.

Although basis B improved the results for OCS from -31.74 MHz (basis A) to -30.92 MHz, the deviation from the experimental value of -29.12 MHz is still surprisingly large. To check, whether this is due to an unsaturated basis or has an another source like, e.g., vibration, we repeated the calculation with the still larger aug-cc-pVTZ basis set by Dunning [61] on C and O. The calculation yielded a value of -30.18 MHz, which proved that the basis set is still not completely saturated. Similarly, replacing the two sets of d-functions on the P of SPF_3 by 3 sets of d-functions (exponents 2.2, 0.55 and 0.1375) and one set of f-functions (exponent 0.45) changed the coupling to -28.89 MHz for basis A and -28.92 MHz for basis B. This shows that two sets of d-functions might not be sufficient as polarization functions for second row elements.

Nuclear Quadrupole Coupling in the Rotational Spectrum of ^{33}S-thiirane

In 1968 Shoemaker and Flygare [5] investigated thiirane with an experimental precision which was

Table 2. Comparison of calculated with experimental ^{33}S quadrupole couplings in MHz.

Molecule	Principal axes of the moment of inertia					Principal axes of χ			Ref. of exp. data	
	Axis	Exp.	Basis A	Basis B	Ref. [23][a]	Axis	Basis A	Basis B	χ	Structure
H_2S	*aa*	-32.82 ± 0.05		-33.35	-33.03	*xx*		-7.56	[24]	[25]
Hydrogen-	*bb*	-8.60 ± 0.07		-7.56	-5.60	*yy*		-33.35		
sulfide	*cc*	41.42 ± 0.06		40.91	38.63	*zz*		40.91		
$H_2S \cdots HF$	*aa*	32.79 ± 0.01		39.21		*xx*		-6.87	[26]	[26]
	bb			-32.49		*yy*		-32.49		
	cc			-6.72		*zz*		39.36		
	ac			2.65						
CH_3SSCH_3	*aa*	-29.65 ± 0.01	-31.01	-31.12		*xx*	-8.03	-7.95	[27]	[28]
Dimethyl-	*bb*	12.81 ± 0.03	13.38	13.41		*yy*	-40.49	-40.53		
disulfide	*cc*	16.84 ± 0.03	17.63	17.72		*zz*	48.52	48.49		
	ab	20.20 ± 0.13	21.79	21.68						
	ac	18.30 ± 0.12	15.44	15.48						
	bc	24.43 ± 0.17	24.29	24.24						
CH_3SCH_3	*aa*	-38.41 ± 0.01		-38.40	-37.17	*xx*		-9.06	[29]	[30]
Dimethyl-	*bb*	-9.73 ± 0.01		-9.06	-7.06	*yy*		-38.40		
sulfide	*cc*	48.14 ± 0.01		47.46	44.23	*zz*		47.46		
CH_3SCN	*aa*	-40.51 ± 0.01	-40.94	-41.01		*xx*	-6.18	-5.90	[31]	[32]
Isothiocya-	*bb*	-7.18 ± 0.01	-6.85	-6.52		*yy*	-41.61	-41.63		
natomethane	*cc*	47.69 ± 0.01	47.79	47.53		*zz*	47.79	47.53		
	ab		4.85	4.65						
C_2H_4S	*aa*	-32.94 ± 0.01		-32.68	-29.62	*xx*		-16.46	this	[33]
Thiirane	*bb*	-16.40 ± 0.01		-16.46	-15.77	*yy*		-32.68	work	
	cc	49.34 ± 0.01		49.14	45.39	*zz*		49.14		
C_3H_6S	*aa*	-12.77 ± 0.01	-13.13	-13.42		*xx*	-15.79	-15.90	[34]	[35]
Methylthiirane	*bb*	-20.34 ± 0.01	-20.27	-20.15		*yy*	-31.87	-31.85		
	cc	33.11 ± 0.01	33.40	33.57		*zz*	47.66	47.74		
	ab		-14.33	-14.24						
	ac		-23.31	-23.33						
	bc		13.04	13.03						
C_4H_8S	*aa*	8.39 ± 0.01	10.29	10.01		*xx*	-14.31	-14.37	[36]	[37]
trans-2,3-di-	*bb*	-32.33 ± 0.01	-32.08	-32.15		*yy*	-32.08	-32.15		
methylthiirane	*cc*	23.94 ± 0.01	21.79	22.15		*zz*	46.39	46.52		
	ac		29.80	29.84						
C_4H_8S	*aa*	-22.64 ± 0.01	-21.18	-21.71		*xx*	-12.66	-13.03	[38]	[39]
2,2-dimethyl-	*bb*	47.18 ± 0.01	46.16	46.44		*yy*	-33.50	-33.41		
thiirane	*cc*	-25.54 ± 0.01	-24.98	-24.73		*zz*	46.16	46.44		
	ac		-10.24	-10.08						
C_4H_4S	*aa*	6.86 ± 0.01	6.25	6.73	6.24	*xx*	6.25	6.73	[40]	[41]
Thiophene	*bb*	-27.81 ± 0.01	-29.41	-28.80	-30.19	*yy*	23.16	22.07		
	cc	20.95 ± 0.01	23.16	22.07	23.95	*zz*	-29.41	-28.80		

advanced at that time. Our studies on methyl substituted thiiranes, like monomethyl- and dimethyl thiiranes [34, 36, 38] convinced us that the ^{33}S-hfs of thiirane [5] itself could presently be investigated with higher precision, as the technique of microwave spectroscopy improved considerably [3]. Thiirane may be used as reference molecule for substituted thiiranes. For symmetry reasons, all off-diagonal elements of the coupling tensor are zero. Rotation of the coupling tensor from the inertial system of thiirane into the inertial systems of substituted thiiranes may therefore serve as reference for the comparison of changes in the electronic environment due to substitution.

The following report may also be taken as an example for many ^{33}S-hfs investigations.

Table 2. Continued

Molecule	Principal axes of the moment of inertia					Principal axes of χ			Ref. of exp. data	
	Axis	Exp.	Basis A	Basis B	Ref. [23]^{a}	Axis	Basis A	Basis B	χ	Structure
C_3H_3NS	*aa*	7.17 ± 0.01	6.64	7.02		*xx*	6.65	7.06	[42]	[43]
Thiazole	*bb*	−26.17 ± 0.01	−27.70	−27.39		*yy*	21.07	20.36		
	cc	19.00 ± 0.01	21.07	20.36		*zz*	−27.71	−27.42		
	ab		−0.60	−1.12						
C_3H_3NS	*aa*	8.70 ± 0.01	8.05	8.38		*xx*	8.70	9.05	[44]	[45]
Isothiazole	*bb*	−32.97 ± 0.01	−34.83	−34.19		*yy*	26.78	25.81		
	cc	24.27 ± 0.01	26.78	25.81		*zz*	−35.49	−34.85		
	ab		−5.33	−5.35						
$(CH_3)_2SO$	*aa*	−15.72 ± 0.02		−16.14	−15.89^{b}	*xx*		−16.14	[46]	[47]
Dimethyl-	*bb*	−17.05 ± 0.02		−17.80	−18.71^{b}	*yy*		−17.95		
sulfoxide	*cc*	32.77 ± 0.03		33.94	34.60^{b}	*zz*		34.08		
	bc			−2.74						
HNCS	*aa*	−27.5 ± 0.8	−28.91	−27.69	−33.16^{b}	*xx*	7.44	6.48	[48]	[49]
Isothtiocyanic	*bb*		7.43	6.46	18.77^{b}	*yy*	21.48	21.23		
acid	*cc*		21.48	21.23	14.38^{b}	*zz*	−28.92	−27.7		
	ab		−0.69	−0.97						
SPF_3	*aa*	−29.92 ± 0.01	−29.12	−29.29	−32.58	*zz*	−29.12	−29.29	[50]	[51]
Thiophos-	*aa*	−28.75 ± 0.40							[51]	
phoryl fluoride										
H_2CS	*aa*	−11.90 ± 0.02		−11.41	−9.68	*xx*		−11.41	[52]	[53]
Thio-	*bb*	49.98 ± 0.01		49.57	45.31	*yy*		−38.15		
formaldehyde	*cc*	−38.08 ± 0.02		−38.15	−35.64	*zz*		49.57		
GeS	*aa*	6.85 ± 0.17		6.46		*zz*		6.46	[54]	[55]
Germanium-										
sulfide										
SO_2	*aa*	−1.7 ± 0.2		−1.31	−0.33	*xx*		−1.31	[56]	[57]
Sulfurdioxide	*bb*	25.71 ± 0.03		26.94	32.72	*yy*		−25.64		
	cc	(−24.01)		−25.64	−32.40	*zz*		26.94		
OCS	*aa*	−29.12 ± 0.01	−31.74	−30.92	−32.06	*zz*	−31.74	−30.92	[58]	[59]
Carbonoxide-										
sulfide										
SCO ··· HF	*aa*	−26.43 ± 0.04	−30.71	−29.81		*zz*	−30.71	−29.81	[60]	[60]
rms deviation between exp. and calc. values				0.96	3.60					

[a] Calculated from electric field gradients in atomic units using the IUPAC value of $-67.8 \cdot 10^{-31}$ m^2 for the nuclear quadrupole moment of ^{33}S.

[b] Values given in the principal axes of the quadrupole coupling (not included in the rms values).

Experiment and Analysis

Thiirane, C_2H_4S, was obtained from Aldrich, Steinheim, and used without further purification. Since for this molecule the transitions with low angular momentum quantum number J are distributed over a wide range, we used molecular beam Fourier transform microwave spectrometers in the range from 6 to 26.5 GHz [62–64] in Kiel and Aachen, and from 26.4 to 40 GHz [65] in Aachen. The instruments introduce the molecular beam parallel to the resonator axis [66], thus increasing resolution, accuracy and sensitivity.

The sample was introduced as a pulsed supersonic molecular beam with a content of 1% in argon and a backing pressure of approximately 50 kPa. 2 K to 20 K experiment cycles were necessary for the ^{33}S transitions. 8 K data points with 40 ns interval were recorded.

As the rotational spectra of the ^{32}S, ^{33}S, and ^{34}S isotopomers were known [5, 33], the low J transitions could easily be identified. Nevertheless we performed a centrifugal distortion analysis for the ^{32}S isotopomer according to van Eijck [67] with the newly measured lines. The centrifugal distortion constants were used for a more precise evaluation of the molecular constants of the ^{33}S isotopomer. We could not record a sufficient number of lines for this rare isotopomer in natural abundance to determine its centrifugal distortion constants. The lines are given in Table 3, the rotational and centrifugal distortion constants in Table 4.

For many ^{32}S- and ^{34}S isotopomer lines a partially resolved fine structure was observed which is not yet interpreted. Spin-rotation or spin-spin coupling may be a source of it. Its analysis needs a still higher resolution. We report in Table 3 for the lines mean values averaged over this fine structure and the Doppler doublets. The lines of the ^{33}S isotopomer measured in natural abundance are given in Table 5. The measured transitions of Table 5 are splitted by nuclear quadrupole coupling. They were analysed by a Hamiltonian of a centrifugally distorted rotor supplemented with ^{33}S nuclear quadrupole coupling [1].

The program HFSC of Gripp [68] used for the evaluation of the parameters diagonalises the hamiltonian matrix. The results are presented in Table 4b.

With the values χ_{gg}, $g = a, b, c$ of the quadrupole coupling constants, included also in Table 2, a reference is available to evaluate substitution effects. A comparison with [5] shows the improved accuracy, by a factor of at least ten, of the presented analysis.

Table 3. Measured transitions of ^{32}S thiirane.

J'	K'_-	K'_+	J''	K''_-	K''_+	ν_{obs}/MHz	$\delta\nu$/kHz
5	2	3	5	2	4	13 142.194	3.7
3	1	2	3	1	3	16 742.397	1.0
2	1	1	2	1	2	8 395.778	0.7
1	0	1	0	0	0	18 851.111	−3.0
4	2	2	4	2	3	6 266.496	3.0
8	3	5	8	3	6	16 059.515	0.6
7	3	4	7	3	5	8 369.644	−9.1
6	2	4	6	2	5	22 976.403	2.9
14	5	9	14	5	10	18 446.861	1.9
13	5	8	13	5	9	10 157.792	−1.0
11	4	7	11	4	8	17 716.394	−1.1
10	4	6	10	4	7	9 581.277	1.4
5	1	4	4	3	1	9 493.513	1.2
4	0	4	3	2	1	16 699.838	−1.5
2	0	2	1	0	1	37 238.217	5.3
2	1	2	1	1	1	34 903.425	−2.9
4	1	3	4	1	4	27 648.269	−5.6
6	0	6	5	2	3	27 995.496	0.5
6	1	5	5	3	2	29 638.557	−0.9
7	2	5	7	2	6	35 515.238	1.2
9	3	6	9	3	7	26 973.155	1.1
12	4	8	12	4	9	29 336.563	−1.2
15	5	10	15	5	11	30 439.378	−0.3

$\delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$, ν_{calc} calculated with constants of Table 4a.

Table 4a. Rotational and centrifugal distortion constants of ^{32}S thiirane.

A /MHz = 21 973.641 (3)
B /MHz = 10 824.892 (1)
C /MHz = 8 026.247 (1)
κ = −0.598686 (1)
D'_J /kHz = 7.052 (18)
D'_{JK}/kHz = 13.76 (14)
D'_K /kHz = 16.62 (28)
δ'_J /kHz = 2.1891 (35)
R'_6 /kHz = −0.42982 (82)
n = 23
σ /kHz = 4.

κ = asymmetry parameter = $(2B - A - C)/(A - C)$, n = number of components, σ = standard deviation, standard errors in parentheses are in units of the last given digit.

Table 4b. Rotational, centrifugal distortion, and quadrupole coupling constants of ^{33}S thiirane.

A /MHz = 21 973.657 (78)
B /MHz = 10 683.79137 (65)
C /MHz = 7 948.35769 (47)
κ = −0.60993 (2)
D'_J /kHz = [7.0520]
D'_{JK} /kHz = [13.757]
D'_K /kHz = [16.625]
δ'_J /kHz = [2.1891]
R'_6 /kHz = [−0.42982]
χ_{aa} /MHz = −32.9424 (78)
$\chi_{bb} - \chi_{cc}$ /MHz = −65.747 (11)
χ_{bb} /MHz = −16.402 (14)
χ_{cc} /MHz = 49.345 (14)
n = 36
σ /kHz = 6.3

The centrifugal distortion constants were fixed to the values of the ^{32}S isotopomer, κ = asymmetry parameter = $(2B - A - C)/(A - C)$, n = number of components, σ = standard deviation, standard errors in parentheses are in units of the last given digit, fixed values in brackets.

Transformation of Coupling Tensors and Discussion

To assist the analysis of a rotational spectrum showing hfs, the tensor of the considered nucleus of a similar molecule is transformed into the principal inertia system of the molecule under investigation [1]. We demonstrate the procedure with thiirane and its methyl derivatives included in this work. The assumption for this procedure is that the structure of the reference molecule and that under investigation is known at least approximately. For the examples given below, r_s- and r_0-structures were determined. The procedure further neglects different surrounding of the coupling nucleus due to substitution effects.

Table 5. Measured transitions of ^{33}S thiirane.

J'	K'_-	K'_+	J''	K''_-	K''_+	F'	F''	ν_{obs}/MHz	$\delta\nu$/kHz
1	0	1	0	0	0	5/2	3/2	18 633.771	−1.1
1	0	1	0	0	0	3/2	3/2	18 625.533	−4.1
1	0	1	0	0	0	1/2	3/2	18 640.359	−2.3
2	1	2	1	1	1	7/2	5/2	34 531.367	0.8
2	1	2	1	1	1	5/2	3/2	34 523.139	7.7
2	1	2	1	1	1	3/2	1/2	34 524.570	8.8
2	1	2	1	1	1	3/2	5/2	34 527.837	−4.1
2	1	2	1	1	1	3/2	3/2	34 531.946	4.0
2	1	2	1	1	1	1/2	3/2	34 544.282	1.8
2	1	2	1	1	1	1/2	1/2	34 536.907	7.4
2	1	2	1	1	1	5/2	5/2	34 519.029	−1.6
2	1	1	2	1	2	7/2	7/2	8 201.450	2.4
2	1	1	2	1	2	5/2	5/2	8 217.881	−4.3
2	1	1	2	1	2	3/2	3/2	8 206.141	−6.6
2	1	1	2	1	2	1/2	1/2	8 189.703	−6.6
2	1	1	2	1	2	7/2	5/2	8 213.786	2.8
2	1	1	2	1	2	5/2	7/2	8 205.536	−14.2
2	1	1	2	1	2	5/2	3/2	8 209.074	−1.2
2	1	1	2	1	2	3/2	5/2	8 214.949	−8.8
2	1	1	2	1	2	3/2	1/2	8 193.806	−3.9
2	1	1	2	1	2	1/2	3/2	8 202.039	−8.6
2	0	2	1	0	1	7/2	5/2	36 825.704	−1.5
2	0	2	1	0	1	5/2	3/2	36 824.101	1.3
2	0	2	1	0	1	3/2	1/2	36 816.304	−1.9
2	0	2	1	0	1	5/2	5/2	36 815.861	−3.7
2	0	2	1	0	1	3/2	3/2	36 831.125	−5.0
2	0	2	1	0	1	1/2	1/2	36 826.143	−2.8
2	0	2	1	0	1	3/2	5/2	36 822.893	−1.6
2	0	2	1	0	1	1/2	3/2	36 840.964	−5.9
3	1	2	3	1	3	9/2	9/2	16 361.719	12.3
3	1	2	3	1	3	7/2	7/2	16 378.027	2.8
3	1	2	3	1	3	5/2	5/2	16 370.404	−6.9
3	1	2	3	1	3	3/2	3/2	16 354.090	−3.9
4	1	3	4	1	4	7/2	7/2	27 048.070	−2.9
4	1	3	4	1	4	11/2	11/2	27 037.730	12.5
4	1	3	4	1	4	9/2	9/2	27 053.668	4.8

$\delta\vartheta = \nu_{obs} - \nu_{calc}$, ν_{calc} calculated with constants of Table 4 b.

The quantum chemical prediction of a coupling tensor relies also on an experimental structure, if it was not optimised. In our cases the r_s-structure was used. In Table 6 we compile for convenience the data for the thiiranes. The rotation of the quadrupole coupling tensor of thiirane in Table 6 was performed with the help of structural data [33, 35, 37, 39].

We give only the magnitude of the off-diagonal elements of the coupling tensor as an analysis of the hfs results in the magnitude of the $\chi_{gg'}$, and the sign of the product $\Pi\, \chi_{gg'}$, $g \neq g'$ [69]. The individual signs of the three or one non zero element is undetermined.

Consideration of Table 6 shows that the values of the coupling constants calculated by quantum chemistry are slightly closer to experimental values than the values obtained by tensor rotation. But the tensor rotation excludes substitution effects, which are noticeable for the example molecules.

Table 2 shows also that experimental and calculated values for dimer complexes disagree more than for the stable molecules. The reason is that the calculated values are for the rigid structure, whereas the experimental values include a zero point vibrational motion mainly of the angle defining the relative position of the two monomers.

In SCO ··· HF, Legon and Willoughby [60] have calculated a zero point vibrational angle θ of 14.36°, assuming no change in the electronics, and applying the equation

$$\chi_{\text{dimer}}/\chi_{\text{monomer}} = \tfrac{1}{2}\langle 3\cos^2\theta - 1\rangle\,.$$

If we take the decrease of χ_{aa} due to electronic influences of −1.11 MHz (Table 2, basis **B**) into account, i.e. increase χ_{dimer} in the above equation by this amount, the above angle decreases to 11°.

Nonlinear complexes, like H_2S ··· HF, need more detailed experimental work to provide at least all χ_{gg}. With the complete set it may be checked if the coupling tensor is changed under complexation. For the example mentioned, especially χ_{bb} is important as it should result from $\chi_{aa}(H_2S)$ if the tensor is not modified by complexation.

An estimate of the electronic influence similar to that for SCO ··· HF, but less accurate, can be made by taking the decrease of 1.55 MHz of the largest tensor element χ_{zz} of the quadrupole coupling in the principal axes of the efg (Table 2, basis **B**). Willoughby et al. [26] calculated an angle of 21.3°, which is increased to 21.9° using the new coupling constants of Saleck et al. [24] for H_2S. Taking into account the above decrease due to electronic effects, this value decreases to 19.7°. This confirms that the assumption was a reasonably good one.

For complexes, an averaging of the coupling tensor over the large amplitude motions should be studied in more detail. The assumption of a coupling tensor invariant to complexation needs verification in each case.

With microwave spectroscopy it is only in rare cases possible to determine the complete coupling tensor in the inertia axis system *a*, *b*, *c*. An example is $CH_3{}^{33}S^{32}SCH_3$ [27]. In many cases the coupling tensor in its own principal axis cannot be determined straight forward. Here quantum chemical calculations are superior. We give in Fig. 2 an illustration for selected examples, where the principal inertia and coupling tensor axes do not coincide. The information results from calculations with basis **B**.

Table 6. Compilation of quadrupole coupling constants χ_{gg} [MHz] in the principal inertia system determined by experiment (exp), by rotation of the quadrupole coupling tensor of thiirane (rot tensor) and by quantum chemical calculations with basis A (QCA) and basis B (QCB).

		Exp.	cit [a]	Rot.-tensor	δ [b]	cit [c]	QCA	δ [b]	QCB	δ [b]
Methylthiirane	χ_{aa}	−12.7731 (82)	[34]	−15.2389	19	[35]	−13.13	3	−13.42	5
	χ_{bb}	−20.3366 (118)		−19.3876	5		−20.27	3	−20.15	1
	χ_{cc}	33.1097 (118)		34.6176	5		33.40	1	33.57	1
	$\lvert\chi_{ab}\rvert$	n.d.		14.8011	–		14.33	–	14.24	–
	$\lvert\chi_{ac}\rvert$	n.d.		24.0623	–		23.31	–	23.33	–
	$\lvert\chi_{bc}\rvert$	n.d.		13.8527	–		13.04	–	13.03	–
2,2-Dimethylthiirane	χ_{aa}	−22.6390 (23)	[38]	−23.0963	2	[39]	−21.18	6	−21.71	4
	χ_{bb}	47.1830 (50)		49.345	5		46.16	2	46.44	2
	χ_{cc}	−24.5440 (50)		−26.2481	7		−24.98	2	−24.73	1
	$\lvert\chi_{ab}\rvert$	n.d.		0	–		0	–	0	
	$\lvert\chi_{ac}\rvert$	n.d.		8.1187	–		10.24	–	10.08	
	$\lvert\chi_{bc}\rvert$	n.d.		0	–		0	–	0	
trans-2,3-Dimethylthiirane	χ_{aa}	8.3871 (93)	[36]	6.5638	22	[37]	10.29	23	10.01	19
	χ_{bb}	−32.3291 (174)		−32.9424	3		−32.08	1	−32.15	1
	χ_{cc}	23.9420 (174)		26.3792	10		21.79	9	22.15	7
	$\lvert\chi_{ab}\rvert$	n.d.		0	–			–		–
	$\lvert\chi_{ac}\rvert$	n.d.		31.3449	–		29.80	–	29.84	–
	$\lvert\chi_{bc}\rvert$	n.d.		0	–			–		–

[a] Citation of experimental values, [b] relative deviation from experimental value in %, [c] citation r_s-structure used for the tensor rotation, n.d. not determined.

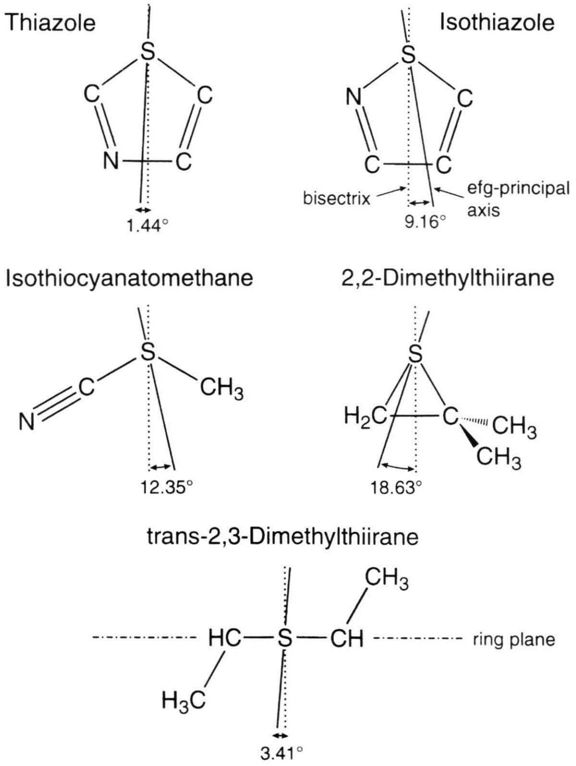

Fig. 2. Calculated deviations of the efg principal axis from the bisectrix in some molecules of the X-S-Y type. For trans-2,3-dimethylthiirane the deviation from the vertical to the ring plane is shown.

Conclusion

It may be stated that the ab initio calculations reproduce the experimental data within the mentioned errors mainly determined by the neglected vibrational contributions. From the still limited number of molecules two groups may be selected, sulfur in a bent bond and sulfur in aromatic systems. Within the groups there are noticeable variations. For other bond types, like sulfoxides and others, the experimental results are very limited. Combination of ab initio calculation and experiment leads presently to the most complete information.

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