Molecular g-Values, Magnetic Susceptibility Anisotropies, Second Moments of the Charge Distribution, and Molecular Electric Quadrupole Moments in trans- and cis-Thioformic Acid

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The rotational Zeeman effect in the microwave spectrum of trans- and cis-Thioformic Acid has been investigated at field strengths upto 25.6 kG. Measurements were done for both $\Delta M = 0$ and $\Delta M = \pm 1$ selection rules for the trans species and for $\Delta M = \pm 1$ for the cis species. From the observed splittings the following parameters were obtained for the diagonal elements of the molecular g tensor and the susceptibility anisotropies.

	trans HCOSH	cis HCOSH
g_{aa}	-0.4091 ± 0.0009	-0.4017 ± 0.0012
g_{bb}	-0.0703 ± 0.0003	-0.0711 ± 0.0004
g_{cc}	-0.0345 ± 0.0003	-0.0318 ± 0.0004
$[2\chi_{aa} - \chi_{bb} - \chi_{cc}] \Big/ \left[\frac{10^{-6}\ \text{erg}}{\text{G}^2\ \text{mole}}\right]$	$-0.67 \quad \pm 0.8$	$-7.32 \quad \pm 1.2$
$[2\chi_{bb} - \chi_{cc} - \chi_{aa}] \Big/ \left[\frac{10^{-6}\ \text{erg}}{\text{G}^2\ \text{mole}}\right]$	$11.37 \quad \pm 0.5$	$16.48 \quad \pm 0.8$

(all experimental uncertinties are single standard deviations).

The molecular electric quadrupole moments derived from the Zeeman data indicate that there is no significant covalent bonding in the O ... H region of the trans species.

Introduction

The study of the high field Zeeman effect in the rotational spectra of diamagnetic molecules is of interest as it gives direct information about the molecular g values and magnetic susceptibility anisotropies. This information, when supplemented by the rotational constants, the structure of the molecule (obtained by normal microwave spectroscopic methods) and by the bulk magnetic susceptibility gives additional molecular parameters such as the diagonal elements of the electric quadrupole moment tensor, the diagonal elements of diamagnetic and paramagnetic susceptibility tensor and if all above informations are fed in, the second moments of the electronic charge distribution.

The present communication reports our investigations on the trans- and cis-species of Thioformic Acid, whose zero field spectrum and molecular structure has recently been reported [1–3].

Experimental

The preparation of the sample has been done by the procedure of Engler and Gattow [4] as modified by Hocking and Winnewisser [1]. The sample was always kept in a glass container at liquid air temperatures and was found to be stable under these conditions. Gaseous samples for spectroscopic (Zeeman) studies were taken by taking away the liquid air container in which the sample tube was immersed and allowing it to warm up until the desired amount of pressure was obtained in the cell. Contrary to the experiences of Hocking and Winnewisser [1], we found that initially the sample decomposed rather fast in our brass wave guide absorption cell, giving it a half life time of only one to two minutes. The half life in the cell could, however, be increased by first warming (upto +90 °C) and pumping off the cell overnight to remove destabilizing impurities from the cell, and then leaving the sample in the cell at a pressure of about 300 m torr and temperature −80 °C for about 12–16 hours. After such a treatment of the cell, the half life of the sample was found to be about two hours, which was sufficient for the present Zeeman work.

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The measurements were done with a conventional 33 kHz Stark effect modulation microwave spectrograph (employing phase stabilized BWO's as radiation sources and an automatic system of recording the frequency markers), which was combined with a strong electromagnet. The spectrograph is equipped with absorption cells of 2.2 meters length for both $\Delta M = 0$ and $\Delta M = \pm 1$ studies and is operating in the frequency range 8.0—40.0 GHz. A detailed description of the spectrograph has been given elsewhere [5, 6]. All measurements have been done at temperatures of about $-50\,°\mathrm{C}$ and the pressure of the gas was kept at about 1—2 m torr to reduce the collision broadening of the absorption lines. Typical recorded half widths at half power points were on the order of 160 kHz. Thus we believe the measurements of the Zeeman splittings to be accurate within ±30 kHz. The magnetic field was measured to an accuracy of better than 0.1% with a Rawson-Lush Type 920 rotating coil gaussmeter, which was calibrated with an nmr gaussmeter.

Theory and Method of Analysis

The effective rotational Hamiltonian of an asymmetric top molecule in the presence of a strong magnetic field $\boldsymbol{H}$ can be written as [6]

$$\begin{aligned}\mathscr{H} &= h(AJ_a^2 + BJ_b^2 + CJ_c^2)\\ &\quad - \mu_N\, \boldsymbol{H}\cdot\tilde{g}\cdot\boldsymbol{J} - \tfrac{1}{2}\,\boldsymbol{H}\cdot\tilde{\chi}\cdot\boldsymbol{H}\\ &\quad - \boldsymbol{\mu}_{\mathrm{el}}\cdot(\boldsymbol{v}_0\times\boldsymbol{H})/c\,,\end{aligned} \tag{1}$$

where

J_a, J_b, J_c are the components of the angular momentum along the principal axes of interia, a, b, and c respectively, (in units of $\hbar$)

A, B, C are the rotational constants,

$\tilde{g}$ is the molecular g tensor,

$\tilde{\chi}$ is the magnetic susceptibility tensor,

$\mu_N = \dfrac{|e|\hbar}{2M_p c}$ is the nuclear magneton,

μ_{el} is the electric dipole moment of the molecule,

v_0 is the velocity of the considered molecule,

c is the velocity of light.

The analysis of the Zeeman patterns was carried out with a computer program in which the above Hamiltonian is handled in the following three steps.

i) The zero field Hamiltonian matrix of the asymmetric rotor is set up with the basis of the eigenfunctions of the limiting symmetric rotor and the eigenvalues and asymmetric top eigenfunctions are determined in the course of a numerical diagonalization.

ii) The matrix elements of the complete Hamiltonian (1) are then calculated in the basis of the asymmetric top functions and the eigenvalues are determined by a perturbation treatment. In view of the smallness of the Zeeman contributions, a first order perturbation treatment was found to be sufficient. Also, the third term, viz. $\mathscr{H}_{\mathrm{TS}}$ has been found to give a significant contribution only for the symmetric top molecules [6], so this can be neglected for the present case, leaving the field dependent contribution to the energy levels as [6, 7]

$$\begin{aligned}E_{\mathrm{H}}(J,\tau,M) &=\\ &-\tfrac{1}{2}\chi H_z^2 - \mu_N \frac{MH_z}{J(J+1)}\sum_g g_{gg}\langle J_g^2\rangle\\ &- H_z^2\,\frac{3M^2 - J(J+1)}{(2J-1)(2J+3)(J+1)J}\sum_g(\chi_{gg}-\chi)\langle J_g^2\rangle\end{aligned} \tag{2}$$

Here J, τ, M are the rotational quantum numbers, $\chi = (1/3)(\chi_{aa} + \chi_{bb} + \chi_{cc})$ is the bulk magnetic susceptibility, χ_{gg} are the diagonal elements of the susceptibility tensor, H_z is the applied magnetic field in the space fixed z-direction, g_{gg} are the diagonal elements of the molecular "g tensor", $\langle J_g^2\rangle$ is the zero field expectation value of the squared angular momentum component along the g-axis.

iii) The molecular g values and susceptibility anisotropies (in this case $2\chi_{aa} - \chi_{bb} - \chi_{cc}$ and $2\chi_{bb} - \chi_{aa} - \chi_{cc}$) are fitted to the observed multiplet splittings by a least square procedure and the results are used to calculate the derived molecular parameters such as the diagonal elements of the electric quadrupole moment tensor etc.

Two examples of observed Zeeman patterns are shown in Figure 1. The measured Zeeman splittings are listed in Table 1 and 2 respectively for the trans- and cis-species of the molecule. The same tables also present the corresponding splittings calculated with the help of the Zeeman parameters of Table 3. Although only the relative signs of the g values can be determined experimentally, it will be shown that the signs mentioned in Table 3 are correct.

Derived Molecular Parameters

With the supplementary information about the structure and bulk magnetic susceptibility of the

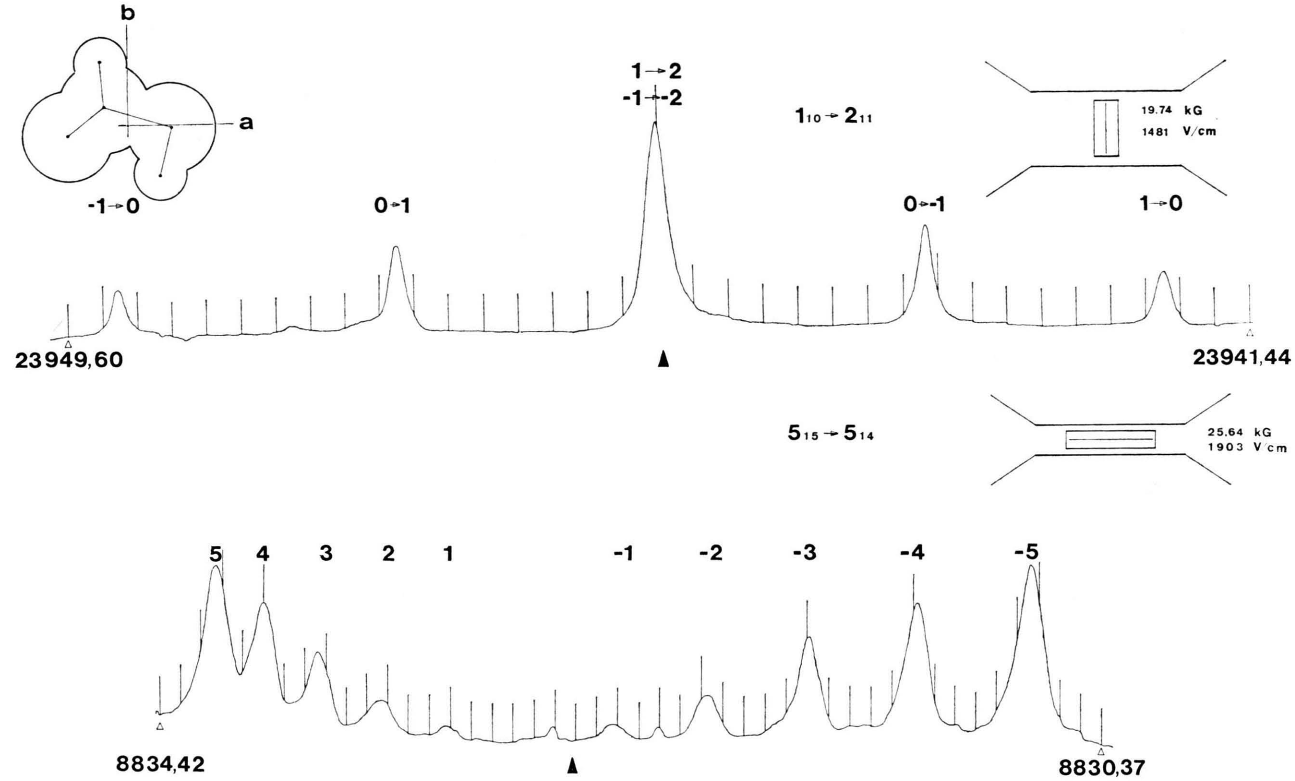

Fig. 1. Observed Zeeman multiplets for the $1_{10} \to 2_{11}$ and the $5_{15} \to 5_{14}$ rotational transitions of trans Thioformic Acid. The inserts show the orientations of the cross section of the waveguide absorption cell in the gap of the magnet. With the electric vector of the microwave perpendicular (upper trace) and parallel (lower trace) to the magnetic fields this leads to $\Delta M = \pm 1$ and $\Delta M = 0$ selection rules respectively. Also given are the magnetic field strengths (in kilo Gauß) and the peak to peak amplitudes of the modulating Stark field (in V/cm). The Zeeman satellites are indicated by the M-values of the lower and upper states. In both spectra the frequency (given in MHz) increases from right to left which was also the sense of registration. [Time constants: $\tau_{\text{RC}} = 1$ sec (upper trace) and $\tau_{\text{RC}} = 3$ sec (lower trace)].

molecule, the parameters mentioned in Table 3 could be used to determine the following quantities as well.

(a) The diagonal elements Q_{gg} of the molecular quadrupole moments. (They are referred to the molecular center of mass).

(b) Each of the diagonal elements χ_{gg} of the susceptibility tensor.

(c) Diagonal elements χ^{p}_{gg} of the paramagnetic and χ^{d}_{gg} of the diamagnetic susceptibility tensors.

(d) Anisotropies of the second moments of the electronic charge distribution.

(e) Individual components of the second moments $\langle 0 | \sum_i g_i^2 | 0 \rangle$ of the electronic charge distribution.

The corresponding equations are [6, 8, 9]

$$Q_{aa} = \frac{|e|}{2}\left[\sum_n^{\text{nuclei}} Z_n (3 a_n^2 - \boldsymbol{r}_n^2) - \left\langle 0 \left| \sum_i^{\text{electrons}} (3 a_i^2 - \boldsymbol{r}_i^2) \right| 0 \right\rangle\right]$$

$$= \frac{-\hbar |e|}{8 \pi M_p}\left\{\frac{2 g_{aa}}{A} - \frac{g_{bb}}{B} - \frac{g_{cc}}{C}\right\} - \frac{2 m c^2}{|e|}\left\{2 \chi_{aa} - \chi_{bb} - \chi_{cc}\right\}, \tag{3}$$

$$\chi_{aa} = \chi^{\text{p}}_{aa} + \chi^{\text{d}}_{aa}, \tag{4}$$

$$\chi^{\text{d}}_{aa.\text{mole}} = N \chi^{\text{d}}_{aa} = \frac{-e^2 N}{4 m c^2}\left\langle 0 \left| \sum_i^{\text{electrons}} (b_i^2 + c_i^2) \right| 0 \right\rangle, \tag{5}$$

$$\chi^{\mathrm{p}}_{aa.\mathrm{mole}} = N\,\chi^{\mathrm{p}}_{aa} = -\frac{e^2 N}{4 m c^2}\left\{\frac{\hbar g_{aa}}{4\pi M_p A} - \sum_n^{\text{nuclei}} Z_n (b_n^2 + c_n^2)\right\} \tag{6}$$

$$\begin{aligned}\langle 0|\sum b_i^2|0\rangle - \langle 0|\sum a_i^2|0\rangle &= \sum_n Z_n (b_n^2 - a_n^2) + \frac{\hbar}{4\pi M_p}\left(\frac{g_{bb}}{B} - \frac{g_{aa}}{A}\right)\\ &+ \frac{4 m c^2}{3 e^2}\{(2\chi_{bb} - \chi_{aa} - \chi_{cc}) - (2\chi_{aa} - \chi_{bb} - \chi_{cc})\}\end{aligned} \tag{7}$$

Table 1. Observed and calculated Zeeman splittings in trans Thioformic acid.

Rotational transition $J_{K-K+} \to J'_{K'-K'+}$	Zero field frequency[a] (MHz)	$M \to M'$	Observed frequency (MHz)	Observed splitting (kHz)	Calculated splitting[b] (kHz)	|Deviation| (kHz)	Magnetic field (kG)
$0_{00} \to 1_{01}$	11694.942	0 0	11694.939	−3	7	12	25.64
$1_{11} \to 2_{12}$	22834.362	−1 −1	22836.608	2246	2220	26	25.64
		0 0	22834.417	55	41	14	
		1 1	22831.969	−2393	−2428	35	
$2_{12} \to 3_{13}$	34248.825	−2 −2	34249.901	1076	1079	1	25.64
		−1 −1	34249.388	563	566	3	
		0 0	34248.821	−4	7	11	
		1 1	34248.219	−606	−598	8	
		2 2	34247.560	−1265	−1274	18	
$2_{11} \to 3_{12}$	35915.539	−2 −2	35916.756	1217	1252	35	25.64
		−1 −1	35916.135	596	600	4	
		0 0	35915.536	−3	−5	2	
		1 1	35914.979	−560	−563	3	
		2 2	35914.470	−1069	−1074	5	
$5_{15} \to 5_{14}$	8332.631	−5 −5	8330.645	−1986	−1984	2	25.64
		−4 −4	8331.139	−1492	−1494	2	
		−3 −3	8331.592	−1039	−1035	4	
		−2 −2	8332.034	−597	−607	10	
		−1 −1	—[c]				
		1 1	—[c]				
		2 2	8333.436	805	794	11	
		3 3	8333.712	1081	1066	15	
		4 4	8333.940	1309	1307	2	
		5 5	8334.148	1517	1519	2	
$6_{16} \to 6_{15}$	11664.392	−6 −6	11662.045	−2347	−2343	4	25.64
		−5 −5	11662.506	−1886	−1872	14	
		−4 −4	11662.968	−1424	−1423	1	
		−3 −3	11663.404	−988	−996	8	
		−2 −2	—[c]				
		−1 −1	—[c]				
		1 1	—[c]				
		2 2	—[c]				
		3 3	11665.501	1109	1105	4	
		4 4	11665.768	1376	1379	3	
		5 5	11666.016	1624	1630	6	
		6 6	11666.242	1850	1859	9	
$0_{00} \to 1_{01}$	11694.942	0 1	11695.726	784	786	2	19.74
		0 −1	11694.167	−775	−790	15	
$1_{10} \to 2_{11}$	23945.530	−1 0	23949.230	3700	3694	6	19.74
		0 1	23947.296	1766	1775	9	
		1 2	23945.507	−23	10	33	
		−1 −2	23945.507	−23	−46	23	
		0 −1	23943.667	−1863	−1861	2	
		1 0	23942.018	−3512	−3519	7	
$1_{11} \to 2_{12}$	22834.362	−1 0	22837.623	3261	3251	10	19.74
		0 1	22835.975	1613	1597	16	
		−1 −2	22834.605	243	254	11	
		1 2	22834.185	−177	−228	51	
		0 −1	22832.893	−1469	−1499	30	
		1 0	22830.950	−3412	−3424	12	

Table 1, (continued)

Rotational transition $J_{K_-K_+} \rightarrow J'_{K'_-K'_+}$	Zero field frequency[a] (MHz)	$M \rightarrow M'$	Observed frequency (MHz)	Observed splitting (kHz)	Calculated splitting[b] (kHz)	|Deviation| (kHz)	Magnetic field (kHz)
$2_{12} \rightarrow 3_{13}$	34248.825	−2 −1	34250.729	1904	1912	8	19.74
		−1 0	34250.344	1519	1527	8	
		0 1	34249.933	1108	1116	8	
		1 2	34249.507	682	677	5	
		2 3	34249.040	215	212	3	
		−2 −3	34248.639	− 186	− 197	11	
		−1 −2	34248.211	− 614	− 628	14	
		0 −1	34247.740	−1085	−1085	0	
		1 0	34247.260	−1565	−1569	4	
		2 1	34246.749	−2076	−2080	4	
$5_{15} \rightarrow 5_{14}$[e]	8332.631	−4 −5	8330.378	−2253	−2277	24	19.74
		−3 −4	8330.716	−1915	−1933	18	
		−2 −3	8331.031	−1600	−1608	8	
		−1 −2	8331.345	−1286	−1301	15	
		0 −1	8331.622	−1009	−1013	4	
		1 0	8331.896	− 753	− 743	10	
		2 1	8332.169	− 462	− 491	29	
		−5 −4			− 343		
		3 2	8332.347	− 284	− 258		
		4 3	—[d]		− 43		
		−4 −3	—[d]		0		
		5 4	—[d]		153		
		−3 −2	8332.939	308	324	16	
		−2 −1	8333.266	635	630	5	
		−1 0	8333.554	923	918	5	
		0 1	8333.824	1193	1187	6	
		1 2	8334.070	1439	1438	1	
		2 3	8334.296	1665	1671	6	
		3 4	—[c]		1885		
		4 5	—[c]		2080		
$6_{16} \rightarrow 6_{15}$[e]	11664.392	−5 −6	—[c]		−2505		19.74
		−4 −5	11662.232	−2160	−2170	10	
		−3 −4	11662.553	−1839	−1848	9	
		−2 −3	11662.860	−1532	−1539	7	
		−1 −2	11663.157	−1235	−1243	8	
		0 −1	11663.437	− 955	− 960	5	
		1 0	11663.708	− 684[f]	− 690		
		−6 −5			− 676		
		2 1	11663.993	− 399[f]	− 434		
		−5 −4			− 341		
		3 2	—[d]		− 190		
		−4 −3	—[d]		− 20		
		4 3	—[d]		41		
		5 4	11664.663	271[f]	259		
		−3 −2			289		
		6 5	—[c]		463		
		−2 −1	11664.958	566	584	18	
		−1 0	11665.256	864	867	3	
		0 1	11665.529	1137	1136	1	
		1 2	11665.786	1394	1392	2	
		2 3	11666.027	1635	1636	1	
		3 4	11666.242	1850	1866	16	
		4 5	11666.462	2070	2083	13	
		5 6	—[c]		2287		

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[a] These have all been remeasured and agree within experimental uncertainty to those reported by Hocking and Winnewisser (Ref. 1).

[b] Calculated with the help of the Zeeman parameters of Table 2.

[c] Too weak to be observed.

[d] Could not be nicely resolved.

[e] Splittings of these transitions were not included in the fitting procedure.

[f] Intensity weighted mean.

Table 2. Observed and calculated Zeeman splittings in cis-Thioformic Acid.

Rotational transition	Zero field frequency[a] (MHz)	$M \to M'$		Observed frequency (MHz)	Observed splitting (kHz)	Calculated splitting[b] (kHz)	|Deviation| (kHz)	Magnetic field (kG)
$0_{00} \to 1_{01}$	11719.005	0	1	11719.776	771	750	21	19.74
		0	−1	11718.213	− 792	− 798	6	
$1_{10} \to 2_{11}$	23987.515	−1	0	23991.205	3690	3664	26	19.74
		0	1	23989.293	1778	1779	1	
		1	2	23987.465	− 50	− 3	47	
		−1	−2	23987.465	− 50	− 90	40	
		0	−1	23985.661	−1854	−1822	32	
		1	0	23984.042	−3473	−3451	22	
$2_{12} \to 3_{13}$	34330.370	−2	−1	—[c]		1878		19.74
		−1	0	34331.835	1465	1494	29	
		0	1	34331.451	1081	1084	3	
		1	2	34330.986	616	647	31	
		2	3	34330.536	166	183	17	
		−2	−3	34330.149	− 221	− 189	32	
		−1	−2	34329.728	− 642	− 604	38	
		0	−1	34329.292	−1078	−1046	32	
		1	0	34328.830	−1540	−1515	25	
		2	1	34328.371	−1999	−2011	12	
$1_{11} \to 2_{12}$	22888.690	−1	0	22891.847	3157	3165	8	19.74
		0	1	22890.297	1607	1591	16	
		1	2	22888.900	210	240	30	
		−1	−2	22888.462	− 228	− 263	35	
		0	−1	22887.298	−1392	−1419	27	
		1	0	22885.387	−3303	−3358	55	

[a] These have all been remeasured and agree within experimental uncertainty to those reported by Hocking and Winnewisser (Ref. 1).
[b] Calculated with the help of the Zeeman parameters of Table 3.
[c] Too weak to be nicely resolved and measured.

Table 3. The molecular values and magnetic susceptibility anisotropy terms in trans- and cis-Thioformic Acid, obtained from the analysis of the measured Zeeman splittings.

Parameter	Trans-Thioformic Acid	Cis-Thioformic Acid	Units
g_{aa}	-0.4091 ± 0.0009	-0.4017 ± 0.0012	—
g_{bb}	-0.0703 ± 0.0003	-0.0711 ± 0.0004	—
g_{cc}	-0.0345 ± 0.0003	-0.0318 ± 0.0004	—
$(2\chi_{aa} - \chi_{bb} - \chi_{cc})_{\text{mole}}$	-0.67 ± 0.8	-7.32 ± 1.2	$\cdot 10^{-6}$ erg/(G^2 mole)
$(2\chi_{bb} - \chi_{aa} - \chi_{cc})_{\text{mole}}$	11.37 ± 0.5	16.48 ± 0.8	$\cdot 10^{-6}$ erg/(G^2 mole)

with cyclic permutations for other components. The results are mentioned in Table 4. The used r_s-structures for both the rotamers have been taken from Ref. [2] and are shown in Figure 2. The sums $\sum_n^{\text{nuclei}} Z_n g_n^2$ over all the nuclei have been included in Table 4 along with the other determined parameters (Z_n = atomic number, $g_n = a_n, b_n, c_n$, coordinates of the n-th nucleus).

To the best of our knowledge, no information is available about the bulk magnetic susceptibility of Thioformic Acid. In the present calculation, this has been estimated using Pascal's empirical method [10] of adding all the concerned atomic susceptibilities in the molecule. The atomic susceptibilities have been taken from Reference [6]. To account for the empirical nature of the method, the uncertainty in χ_{mole} was put as $\pm 5 \cdot 10^{-6}$erg/(G^2mole).

Discussion

From the measured Zeeman splittings one gets only the relative signs of the components of the g tensor. This is due to the fact that with the reversed signs of the g components, the Zeeman

Table 4. Derived molecular parameters for trans- and cis-Thioformic Acid.

Parameter	Units	trans-Thioformic Acid	cis-Thioformic Acid
Q_{aa}	$\cdot 10^{-26}$ esu cm^2	$-$ 5.0 $\pm$ 0.6	$-$ 1.3 $\pm$ 0.8
Q_{bb}	$\cdot 10^{-26}$ esu cm^2	$-$ 5.8 $\pm$ 0.5	4.1 $\pm$ 0.8
Q_{cc}	$\cdot 10^{-26}$ esu cm^2	$-$ 0.8 $\pm$ 0.9	$-$ 2.8 $\pm$ 1.2
$\chi = (\chi_{aa} + \chi_{bb} + \chi_{cc})_{\text{mole}}/3$	$\cdot 10^{-6}$ erg/(G^2 mole)	$-$ 26.5 $\pm$ 5.0*	$-$ 26.5 $\pm$ 5.0*
χ_{aa} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	$-$ 26.7 $\pm$ 5.3	$-$ 28.9 $\pm$ 5.3
χ_{bb} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	$-$ 22.7 $\pm$ 5.2	$-$ 21.0 $\pm$ 5.2
χ_{cc} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	$-$ 30.0 $\pm$ 5.4	$-$ 29.5 $\pm$ 5.4
$\sum_n Z_n a_n^2$	$\cdot 10^{-16}$ cm^2	41.82	42.70
$\sum_n Z_n b_n^2$	$\cdot 10^{-16}$ cm^2	6.19	5.83
$\sum_n Z_n c_n^2$	$\cdot 10^{-16}$ cm^2	0.0	0.0
χ^{p}_{aa} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	40.3 $\pm$ 0.5	38.3 $\pm$ 0.7
χ^{p}_{bb} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	201.9 $\pm$ 0.5	205.9 $\pm$ 0.7
χ^{p}_{cc} mole	$\cdot 10^{-6}$ erg/(G^2 mole)	216.9 $\pm$ 0.5	218.1 $\pm$ 0.7
$\langle a^2 \rangle - \langle b^2 \rangle$	10^{-16} cm^2	37.1 $\pm$ 0.3	37.6 $\pm$ 0.3
$\langle b^2 \rangle - \langle c^2 \rangle$	10^{-16} cm^2	5.3 $\pm$ 0.3	4.9 $\pm$ 0.3
$\langle c^2 \rangle - \langle a^2 \rangle$	10^{-16} cm^2	$-$ 42.4 $\pm$ 0.3	$-$ 42.5 $\pm$ 0.3
χ^{d}_{aa} mole	10^{-6} erg/(G^2 mole)	$-$ 67.0 $\pm$ 5.7	$-$ 67.2 $\pm$ 6.0
χ^{d}_{bb} mole	10^{-6} erg/(G^2 mole)	$-$224.6 $\pm$ 5.7	$-$226.9 $\pm$ 6.0
χ^{d}_{c} mole	10^{-6} erg/(G^2 mole)	$-$247.0 $\pm$ 6.0	$-$247.6 $\pm$ 6.8
$\langle a^2 \rangle$	10^{-16} cm^2	47.7	48.0
$\langle b^2 \rangle$	10^{-16} cm^2	10.5 $\pm$ 2.1	10.4 $\pm$ 2.3
$\langle c^2 \rangle$	10^{-16} cm^2	5.3	5.5

* Estimated from Pascal‘s empirical method of adding all the concerned atomic susceptibilities in the molecule. Uncertainty of $\pm$ 5.0 is mentioned to take into account the empirical nature of its determination.

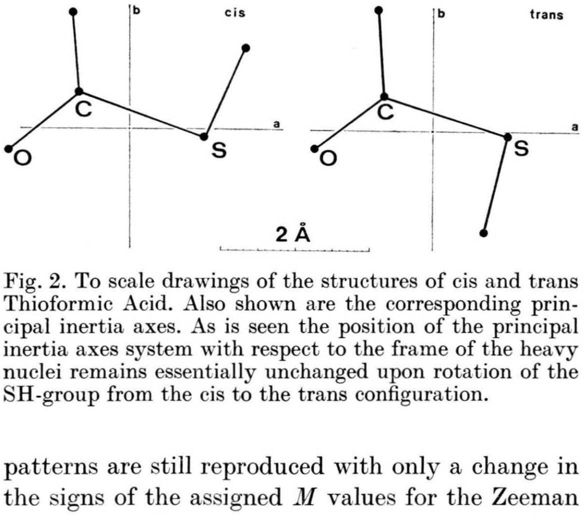

Fig. 2. To scale drawings of the structures of cis and trans Thioformic Acid. Also shown are the corresponding principal inertia axes. As is seen the position of the principal inertia axes system with respect to the frame of the heavy nuclei remains essentially unchanged upon rotation of the SH-group from the cis to the trans configuration.

patterns are still reproduced with only a change in the signs of the assigned M values for the Zeeman components. From the experimental point of view, the absolute sign of the g components can be conclusively determined, if one can work with circularly polarized microwaves and thus distinguish between the $\Delta M = +1$ and $\Delta M = -1$ components of the Zeeman pattern. However, in our case, this correct sign could also be determined in the following way. As mentioned in the previous section, one determines the second moment of the electronic charge distribution for both the sets of signs of the g components. The results are given in Table 5. One might rule out the alternative II (all positive g components) in both rotamers on the basis that it would give a negative value for the quantities $\langle 0 | \sum_i c_i^2 | 0 \rangle$, whereas these should be positive definite quantities. However, one has to do it with some caution, as the projected uncertainties in its value may surpass and make it slightly positive. At this point it may be worthwhile to compare the observed $\langle 0 | \sum_i c_i^2 | 0 \rangle$ value with a calculation based on the additivity rule for $\langle c^2 \rangle$ as proposed by Flygare and coworkers [11]. This proposes a contribution of 0.25 Å^2 from the zeroth row atoms of the periodic table (H and He) [11], of 1.0 Å^2 from the atoms of the first row [11] and 2,5 Å^2 from sulphur [12]. A simple calculation of this kind gives a value of 5.0 Å^2 for $\langle c^2 \rangle$ for Thioformic Acid. This compares nicely with the observed values in both the rotamers with alternative I (all g components negative). Even with the projected uncertainties, it will be hard to think that alternative II would be compatible with such a large positive value for $\langle 0 | \sum_i c_i^2 | 0 \rangle$.

Table 5. Calculated values of the second moment of electronic charge distribution for both the rotamers of Thioformic Acid and for both the possible sets of signs for the components of the g tensor[a].

	trans HCOSH		cis HCOSH	
	I[b]	II[c]	I[b]	II[c]
$\langle 0 \vert \sum_i a_i^2 \vert 0 \rangle$	47.7	42.1	48.0	42.5
$\langle 0 \vert \sum_i b_i^2 \vert 0 \rangle$	10.5 ± 2.1	9.9 ± 2.1	10.4 ± 2.3	10.1 ± 2.3
$\langle 0 \vert \sum_i c_i^2 \vert 0 \rangle$	5.3	− 0.7	5.5	− 0.7

[a] All numbers are in units of 10^{-16} cm^2.
[b] Calculated with all negative g components.
[c] Calculated with all positive g components.

Sometimes a comparison of the derived diagonal elements of the electric quadrupole moment tensor with those known for similar molecules is also used to ascertain the correct choice of sign for the components of the g tensor. Again the conclusions reached for trans-Thioformic Acid by comparing the electric quadrupole moment components to those of trans-Formic Acid is in favour of alternative I. Unfortunately this cannot be done for cis-Thioformic Acid as Formic Acid [13] has not yet been detected in the cis form in the gaseous phase, at least not by microwave spectroscopy.

A complete description of the diagonal elements in the magnetic susceptibility tensor has been obtained in both of the rotamers. There is little difference in the diagonal elements of the total magnetic susceptibility for the cis and the trans forms of the molecule. The partial reason of this may be that the change in the position of the Hydrogen atom from the trans to the cis configuration alters only slightly the relative orientation of the principal axes system of the molecule (see Figure 2). These diagonal elements are similar to the corresponding principal axes values in Acetaldehyde [14] ($\chi_{aa} = -20.0$, $\chi_{bb} = -19.5$, $\chi_{cc} = -28.6$) and Formic Acid [14] [$\chi_{aa} = -18.6$, $\chi_{bb} = -16.8$, $\chi_{cc} = -24.2$, all in units of 10^{-6} erg/(G^2 mole)].

The in plane molecular quadrupole moments in trans-Thioformic Acid are also similar to those for trans-Formic Acid. The large negative value is along a line which passes approximately through the Oxygen and Sulphur atoms. The large positive value is along a line which passes near to both the Hydrogen atoms. Thus it is evident that the negative charge builds up at the oxygen and the sulphur extremities and positive charge shows up at the hydrogen extremities. This is in agreement with the known electronegativity scale of Pauling [15]:

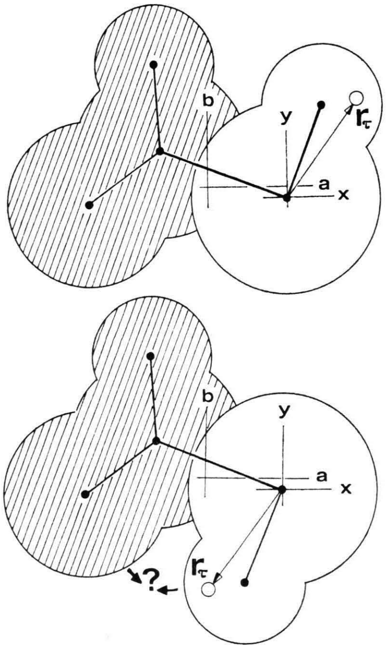

Fig. 3. The prediction of the changes of the components of the quadrupole moment tensor is based upon the simplified model of rigid charge distributions for the frame (shaded area) and for the SH-group (light area), the latter assumed to have cylindrical symmetry about the SH axis. If the bond angle ∢ CSH is also approximated by 90°, the change in position for volume elements of the SH group carrying equivalent charges is given by:

cis-configuration	trans configuration
$a_\tau = a_S + x_\tau$	$a_\tau = a_S - x_\tau$
$b_\tau = b_S + y_\tau$	$b_\tau = b_S - y_\tau$
$c_\tau = z_\tau$	$c_\tau = z_\tau$

(a_S, b_S = a- and b-coordinates of the Sulfur atom. The a- and b-coordinates of the heavy nuclei remain essentially unchanged upon rotation of the SH-group.) This transformation together with the definitions for the bond dipole moment and the molecular quadrupole moments lead to Eqs. (8) in the text.

For a discussion of the change of the components of the quadrupole moment tensor upon rotation of the SH group from the cis to the trans configuration we make use of the fact that the CSH-bond angle is very close to 90°. This makes it possible to relate the two sets of quadrupole moments via the *a*- and *b*-coordinates of the Sulfur atom and the electric dipole moment of 0.8 Debye attributed to the SH-bond [3, 13].

$$\begin{aligned} Q_{aa\,\mathrm{trans}} &\overset{!}{=} Q_{aa\,\mathrm{cis}} - (4 \cdot a_{\mathrm{S}} \cdot \mu_{a\mathrm{SH}} - 2 \cdot b_{\mathrm{S}} \cdot \mu_{b\mathrm{SH}}) \\ &\overset{!}{=} Q_{aa\,\mathrm{cis}} - (4 \cdot 1.04 \cdot 0.34 + 2 \cdot 0.08 \cdot 0.73)\ \mathrm{esu}\ \text{Å}^2 \\ &\overset{!}{=} Q_{aa\,\mathrm{cis}} - 1.5\ \mathrm{esu}\ \text{Å}^2, \\ Q_{bb\,\mathrm{trans}} &= Q_{bb\,\mathrm{cis}} - (4 \cdot b_{\mathrm{S}} \cdot \mu_{b\mathrm{SH}} - 2 \cdot a_{\mathrm{S}} \cdot \mu_{a\mathrm{SH}}) \\ &\overset{!}{=} Q_{bb\,\mathrm{cis}} - (-4 \cdot 0.08 \cdot 0.73 - 2 \cdot 1.04 \cdot 0.34)\ \mathrm{esu}\ \text{Å}^2 \\ &= Q_{bb\,\mathrm{cis}} + 0.9\ \mathrm{esu}\ \text{Å}^2 . \end{aligned} \tag{8}$$

Equations (8) directly follow from the definitions for the electric dipole and quadrupole moments, if one assumes rigid charge distributions for both the frame of the molecule and the SH-group, if one neglects the slight changes in the orientation of the principal inertia axes system with respect to the frame of the heavy nuclei, and if one approximates the rotation about the CS-band by a 180° rotation about an axis running parallel to the molecular *c*-axis through the Sulfur atom (see Figure 3). As is seen by comparison to Table 4, the changes predicted from Eqs. (8) are indeed in the correct direction, but the experimentally found changes are larger by a factor of about two. From the point of view of Hydrogen bonding this finding is unexpected since any covalent contribution to a O...H bond should shift some electron charge from the Oxygen and Hydrogen atoms into the O...H region which should make Q_{aa} more positive and Q_{bb} more negative than predicted by Equations (8). For instance a shift of -0.25 esu from O and H into the center of the O...H region, roughly equivalent to 5% covalent bonding, would lead to an increase of Q_{aa} by 0.6 esu Å^2 and to a slight decrease of Q_{bb} by 0.2 esu Å^2.

Thus, as is obvious from the data, the experimentally found quadrupole moments do not support the idea of covalent bond contributions in the O...H region. It is however also evident, that a discussion of Hydrogen bonding based upon experimental Q-values requires a higher experimental accuracy which is not easily achieved from Zeeman studies, since the well determined leading digits of the g-values drop out in Eqs. (3) used to calculate the Q-values.

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