Determination of the Structure of Monothioformic Acid by Microwave Spectroscopy

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Summary The ground vibrational state rotational spectra of two planar rotational isomers of monothioformic acid, HCOSH, have been measured and assigned in the microwave and millimetre wave regions.

MONOTHIOFORMIC ACID could exist in one or more of four different planar forms, namely the *trans*- and *cis*-isomers of HC(:O)SH and HC(:S)OH Although non-planar configurations are possible, they are unlikely in view of the known planarity of formic acid,[1] which exists only as the *trans*-isomer. The preparation of monomeric monothioformic acid has recently been reported,[2] and the i.r. and ^{1}H n.m.r. spectra of the liquid have both been interpreted as arising from the HC(:O)SH form.[3] These investigations, however, gave no indication as to whether one or more rotamers were present.

In cases where microwave spectroscopy can be applied to the investigation of rotational isomerism it appears to be the most suitable technique, since each isomer exhibits a unique rotational spectrum which can be directly related to its structure. We have therefore investigated the rotational spectrum of monothioformic acid and begun the study of its various isotopic species to obtain precise structural information.

The samples of monothioformic acid were prepared following essentially the procedure outlined by Engler and Gattow.[3] The spectra were recorded at room temperature using a Hewlett-Packard 8460A MRR spectrometer and a previously described millimetre wave spectrometer.[4]

Two distinct but similar rotational spectra were found. The species, (I) and (II), giving rise to these spectra were always present in roughly equal amounts. For each of the two species more than 40 transitions have been measured and assigned. These include a-type R- and Q-branch transitions as well as b-type transitions belonging to the $K_a = 1 \leftarrow 0$, $2 \leftarrow 1$, $3 \leftarrow 2$, and $4 \leftarrow 3$ rotational sub-bands.

TABLE

Rotational constants[a] in MHz, moments of inertia and inertial defect[b] in a.m.u. Å^2 of monothioformic acid

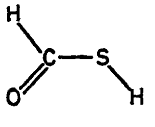
	Species (I)	Species (II)
A_0	62,036·112(19)	62,927·723(9)
B_0	6125·3056(5)	6134·2606(8)
C_0	5569·6437(5)	5584·7539(8)
I_a	8·146,722,3	8·031,293,0
I_b	82·508,696	82·388,247
I_c	90·740,271	90·494,763
Δ	0·084,853	0·075,223

[a] Figures in parentheses are standard errors in units of the last significant figures. 35 transitions of species (I) and 38 transitions of species (II) with $J \leqslant 29$ were used in the analyses.

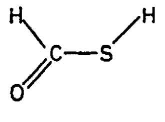
[b] $\Delta = I_c - I_b - I_a$.

Centrifugal distortion analyses were carried out on the two sets of frequencies using the least-squares method.[5] In both cases, the centrifugal distortion effects were found to be small. Only quartic terms had to be included in the Hamiltonian to fit the spectra for $J < 30$ with a standard deviation of 17 kHz for species (I) and 24 kHz for species (II). The resultant accurately determined rotational constants, the principal moments of inertia, and the inertial defects are given in the Table.

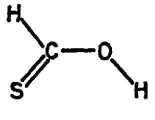
The small positive values obtained for the inertial defect indicate that both species are planar. Furthermore, they must be quite rigidly planar in view of the small centrifugal distortion effects, the absence of any strong vibrational satellites and the lack of internal rotation splittings in any of the observed ground vibrational state transitions.



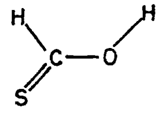
trans-HC(:O)SH



cis-HC(:O)SH



trans-HC(:S)OH



cis-HC(:S)OH

Structural calculations were made in order to determine which of the four possible isomers of monothioformic acid were producing the observed spectra. With all other parameters fixed,[6] the CS internuclear distance and the OCS angle were varied in each of the four possible isomers until the calculated values of the rotational constants A_0 and B_0 agreed with the observed ones for either species (I) or (II). This procedure established that the two HC(:O)SH isomers were the most likely, but it did not completely eliminate the HC(:S)OH isomers and so we sought further evidence from isotopically substituted species. For each isomer several low J-transitions were assigned for both the ^{34}S species (observed in natural abundance) and the acid-deuteriated species HC(:O)SD. The measured isotopic shifts clearly established that spectrum (I) was due to the *trans*-isomer of HC(:O)SH and spectrum (II) to the *cis*-isomer of HC(:O)SH. With this assignment preliminary values were then calculated for the CS internuclear distance and the OCS angles using the following assumed values for the remaining parameters:[6] r(CO) 1·228, r(CH) 1·097; r(SH) 1·325 Å; ∠ (HCS) 110, ∠ (HSC) 92°. The results are: r(CS) 1·760 Å, ∠ (OCS) 125·7° in *trans*-HC(:O)SH and r(CS) 1·760 Å, ∠ (OCS) 123·1° in *cis*-HC(:O)SH.

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