

Short Communications

Force Field of Ethylthiocyanate*

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The vibrational spectra and conformation of ethylthiocyanate have been of interest to several research groups during the last years. A thorough analysis of the vibrational spectrum was done by Hirschman *et al.*,¹ who interpreted the spectrum on the basis of two rotational isomers, *anti* (with C_s symmetry) and *gauche* (C_1 symmetry). The *anti*-form was found to be the more stable. Crowder² calculated a force field which reproduces most of the observed frequencies, based on the *anti*-conformation. From a recent microwave investigation³ of ethylthiocyanate, however, it was concluded that the *gauche* form was the more stable, and no lines originating from the *anti* conformer were assigned. This led to a reinvestigation⁴ of the IR-spectrum in the solid (crystalline and amorphous), liquid, and vapour phase and the liquid Raman spectrum. This work concludes that all bands in all states can be ascribed to one isomer only, and that the polarization data and vapor phase contours indicate that this rotamer is the *gauche* isomer. In the present communication the determination of the force field based on the *gauche* conformation is reported.

Method of calculation. The normal coordinate program used in this work is described by Gwinn.⁵ In this program mass weighted cartesian coordinates are used and rotation and translation are not separated until the matrix diagonalization is performed. The V matrix is generated numerically and only one transformation, from cartesian to normal coordinates, is involved.

In the initial calculations a valence force field

$$V = \frac{1}{2} \sum K_{ij} (\Delta r_{ij})^2 + \frac{1}{2} \sum H_{ijk} (\Delta \phi_{ijk})^2 + \frac{1}{2} \sum Y_{ijkl} (\Delta t_{ijkl})^2$$

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was used, where the diagonal force constants K , H , and Y represent stretching, bending, and torsion, respectively. In many cases, redundant internal coordinates are used, *i.e.* the three H_{CCH} and three H_{HCH} of the methyl group. During the transformation to the basis of cartesian displacement coordinates these redundancies are removed automatically. Likewise, the torsional force constant is read for all H C C H combinations in the ethyl group, *i.e.* $9Y_{HCCH}$ force constants (with the same value). To improve the agreement between observed and calculated frequencies it was found necessary to introduce interaction constants, defined as F^1 for interaction between two stretching force constants, F^2 between stretching and bending, and F^3 between two bending force constants. The structure of the molecule was taken from the microwave work.³

Table 1. Force constants of CH_3CH_2SCN .

Force constant	Value ^a
$K_{C \equiv N}$	16.73
$K_{S-C \equiv}$	3.72
K_{CS}	2.65
K_{CH}	4.73
K_{CC}	4.70
H_{SCN}	0.392
H'_{SCN}	0.369
H_{CSC}	0.68
H_{SCC}	1.16
H_{SCH}	0.66
$H_{CCH}(CH_2)$	0.56
$H_{CCH}(CH_3)$	0.66
$H_{HCH}(CH_2)$	0.50
$H_{HCH}(CH_3)$	0.54
Y_{SC}^b	0.02
Y_{CC}	0.0114
$F^1_{CH,CH}(CH_2)$	0.10
$F^1_{CS,SC}$	0.30
$F^2_{CC,CCH}(CH_3)$	0.51
$F^2_{SC,SCH}$	0.35
$F^2_{SCH,SCH}$	-0.125
$F^3_{HCH,HCH}(CH_3)$	0.015
$F^3_{SCH,CCH}(CH_2)$	-0.015

^aUnits are mdyn/Å for K and F^1 , mdyn for F^2 and mdynÅ for H , Y , F^3 . ^bTransferred from Ref. 8.

Results and discussion. The force field defined above is very convenient from a practical point of view since force constants can be transferred between similar molecules.⁶ For simplicity the force field of methylthiocyanate was calculated first. The results are in good agreement with those previously published by Crowder² and Lett and Flygare.⁷ The force field of ethylthiocyanate is listed in Table 1. The force constants are quite similar to those of methylthiocyanate and of thioalkanes.⁸ The calculated and observed frequencies are listed in Table 2 together with an approximate description of the vibrations. With a few exceptions, the assignments are the same as reported in Ref. (4). The bands

Table 2. Observed and calculated frequencies and approximate description of vibrations in $\text{CH}_3\text{CH}_2\text{SCN}$.

Observed ^a (cm^{-1})	Calculated (cm^{-1})	Approximate description
2999	2999.1	CH_3 asym. str.
2984	2988.7	CH_3 asym. str.
2948	2961.2	CH_3 asym. str.
2946 ^b	2949.5	CH_3 sym. str.
2888	2880.3	CH_3 sym. str.
2170	2170.1	CN str.
1456	1463.1	CH_3 scissor
1456	1451.4	CH_3 scissor
1434	1436.9	CH_3 scissor
1389	1386.2	CH_3 sym. def.
1283	1272.6	CH_2 wag
1244 ^b	1248.1	CH_3 twist
1066	1058.2	CH_3 rock
1049 ^b	1046.2	CH_3 rock
971	971.8	CC str.
774	793.6	CH_3 rock
675	685.4	CS str.
640	640.8	$\text{SC}\equiv\text{N}$ str.
453 ^c	453.0	SCN bend
394	393.8	SCN bend
326	323.6	CCS bend
249 ^b	249.8	CH_3 torsion
149	149.9	CSC bend
—	72.2 ^d	C—S torsion

^aObserved frequencies taken from Ref. 4. Unless marked, IR vapour phase values. ^bLiquid IR value. ^cLiquid Raman value. ^dThis calculated frequency depends mainly on the transferred force constant value for Y_{SC} .

at 453 and 394 cm^{-1} were assigned to C—C—S bend and the bands at 326 and 308 cm^{-1} as S—C \equiv N bend. The calculations clearly indicate that the S—C \equiv N bending vibrations are the ones previously assigned as C—C—S bend (453 and 394 cm^{-1}) and that the C—C—S bend is at

326 cm^{-1} . This is more in accordance with the assignment of the corresponding vibrations in methylthiocyanate, where the two S—C \equiv N bending vibrations are 460 and 389 cm^{-1} .^{9,10} In $\text{CH}_3\text{CH}_2\text{SCH}_3$ ¹¹ the CCS vibration is observed at 335 cm^{-1} , which also is in agreement with the reassignment of these vibrations. Using the force constants found for the C—S torsion reported for several thioalkanes,⁸ this vibration was calculated to be 72 cm^{-1} , in accordance with the value calculated by Ohsaku *et al.*¹¹ for the C—S torsion in $\text{CH}_3\text{CH}_2\text{—SCH}_3$. Only one vibration was observed below 200 cm^{-1} , the CSC bend at 149 cm^{-1} . Although it is not very likely, it is possible that there is an overlap of the C—S torsion and the CSC bending at this frequency. The possibility also exists that, despite the thorough studies both in infrared and Raman, the lowest fundamental vibration is still not observed.

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