On the Structure of Ethyl Mercaptan

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Recently, Kadzhar, Abbasov, and Imanov[1] have published a paper on the microwave spectra of trans ethyl mercaptan and its ^{34}S isotopically-substituted species. We have also independently worked on the same molecule and five isotopically-substituted species, in both the trans and gauche molecular forms.

For the trans isomer, since we have not yet finished the measurements of two ^{13}C isotopic species, the r_s structure of the molecule can not be obtained at present. A preliminary survey has shown us, however, that too many weak spectra crowd around the expected regions for the ^{13}C species, and careful measurements will be necessary for the assignment of the spectra due to two ^{13}C species in natural abundance. Therefore, we have obtained only a tentative structure which reasonably reproduces the observed rotational constants.

For the gauche isomer, we could assign the spectra only to "a"-type transitions. For "b"- and "c"-type spectra, the splittings due to the internal rotation of the SH group seem to be too large for us to get the reasonable assignments without information from theoretical treatments of the splittings, on which we are now working.

The "a" type spectra of the $J_{0J}\rightarrow(J+1)_{0J+1}$ type show no splitting, while the spectra of the $J_{1J}\rightarrow(J+1)_{1J+1}$ and $J_{1J-1}\rightarrow(J+1)_{1J}$ types are split into doublets, with separations of several mega-Hertz.

The "B" and "C" rotational constants shown in the table can be obtained by taking the average frequencies of the components of the doublets for the latter types of the spectra.

As for the "A" rotational constants, we cannot obtain them from the "a"-type spectra alone since the molecule is so close to the symmetric top. The observed rotational constants of the gauche isomer are not reproduced by simply changing the dihedral angle CCSH, while keeping the other structural parameters the same as those of the trans form; the discrepancies amount to about 5% for all isotopic species. However, reasonable agreements are obtained if we change the dihedral angle CCSH after exchanging the values of the CCS and one of the CCH angles in the CH_2 group. The CCH angle to be exchanged is the one situated at the trans position against the SH bond in the gauche isomer.

This is understandable if we have a tilted CH_2 group toward the SH bond; it is similar to the CH_3 group found, for example, in methyl mercaptan.[2]

trans isomer	(MHz)	A	B	C
CH_3CH_2SH		28416.74 (9.02)[a]	5485.90 (4.08)	4882.00 (−6.32)
CH_3CH_2SD		27155.69 (30.39)	5304.20 (2.51)	4702.47 (−7.51)
$CH_3CH_2{}^{34}SH$		28330.09 (9.39)	5367.24 (3.40)	4785.07 (−6.20)
CH_3CD_2SH		22275.10 (−5.12)	5342.46 (−2.03)	4691.21 (−16.42)
CH_2DCH_2SH	sym	28386.99 (24.49)	5095.23 (1.94)	4570.14 (−7.15)
	asym	25913.56 (0.32)	5293.75 (3.07)	4714.34 (−7.06)

gauche isomer	(MHz)	B	C
CH_3CH_2SH		5294.25 (267.27)[b] (10.34)[c]	4846.99 (155.02) (−5.97)
CH_3CH_2SD		5190.01 (262.18) (12.78)	4768.69 (153.55) (−6.72)
$CH_3CH_2{}^{34}SH$		5174.52 (259.99) (9.54)	4745.63 (152.60) (−5.90)
CH_3CD_2SH		5165.02 (237.27) (1.25)	4665.73 (120.59) (−16.17)
CH_2DCH_2SH	sym	4925.07 (237.16) (7.49)	4534.85 (141.77) (−6.09)
	asym-1	5107.18 (255.20) (0.35)	4680.53 (154.02) (−7.21)
	asym-2	5112.46 (270.34) (14.79)	4666.62 (157.61) (−3.63)

CH_3	r(CH)	1.091 Å	∠HCH	108°00′	∠CCH	110°56′		
CH_2	r(CH)	1.091 Å	∠HCH	107°00′	∠CCH	108°12′	∠HCS	113°05′
skeleton	r(CC)	1.535 Å	r(CS)	1.819 Å	r(SH)	1.328 Å		
	∠CCS	108°32′	∠CSH	96°35′				

a) calcd − obsd

b) calcd − obsd assuming the same structural parameters for the *trans* isomer except the dihedral angle CCSH which was taken as 60°.

c) calcd − obsd assuming the exchange of the CCS and one of the CCH angles and the change of the dihedral angle CCSH from 180° to 60° keeping the other structural parameters unchanged.

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1) Ch. O. Kadzhar, A. A. Abbasov, and L. M. Imanov, *Optics and Spectry.*, **24**, 334 (1968).

2) The summary of the references is shown in L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961).