

## Fourier Transform Microwave Spectra of Isobutylmercaptan and Normal Butylmercaptan

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In order to obtain information on stable conformations and internal motions of isobutylmercaptan (2-methyl-1-propanethiol) and normal butylmercaptan, we have analyzed their rotational spectra observed by Fourier transform microwave spectroscopy. We may expect that isobutylmercaptan exists in five stable rotational isomers, that is, there are two configurations around the  $\text{CH}(\text{CH}_3)_2 - \text{CH}_2\text{SH}$  bond referred to as *gauche* and *trans* and more than two minima on the internal rotation of the SH group, whereas more than ten stable conformations will be present in normal butylmercaptan.

We scanned the frequency region from 3.7 to 25 GHz using a sample of isobutylmercaptan diluted in Ar to 0.5%. We assigned the observed spectra to two *gauche* forms,  $G_1$  and  $G_2$ , and one *trans* form  $T_1$ : *a*-, *b*-, and *c*-type transitions for the  $G_1$  and *a*- and *c*-type transitions for the  $G_2$ , whereas no *b*-type transitions were observed for  $G_2$ . The  $G_1$  spectra were found stronger than those of  $G_2$ . These observations could be explained by the S-H and C-S bond moments. All the three types of transitions were detected for  $T_1$ , of which all *b*-type lines appeared as doublets with the spacing of about 13 MHz. This splitting was ascribed to the tunneling of the SH group through a potential barrier on the *a*-*c* plane between two equivalent minima.

*Ab initio* calculations at the MP2/6-311++G(*d*, *p*) level demonstrated that for isobutylmercaptan there were two minima for the *gauche* form at the CCSH dihedral angle of 72.2° and 298.1°, which corresponded to  $G_1$  and  $G_2$ , as observed, whereas two equivalent minima at the CCSH dihedral angles of either 73.8° or 286.2° were for the *trans* form, in good accord with the experimental observations.

For normal butylmercaptan we scanned the frequency region from 5 to 20 GHz. We assigned *a*-type transitions from  $J = 2 \leftarrow 1$  to  $J = 7 \leftarrow 6$  to four conformers and *b*- and *c*-type transitions to two of the four conformers. The spectra of these two were of second and third strongest among others. The rotational constants and inertial defects,  $I_{cc} - I_{aa} - I_{bb}$ , which were derived from the observed spectra, indicated that the conformer with the strongest spectra had a planar *trans* heavy-atom skeleton, but perhaps the SH hydrogen out of the skeletal plane. Most of the *a*-type  $K = 1$  transitions of this species were found split into doublets. The second and third conformers probably take *gauche* conformations with respect to the  $\text{CH}_2 - \text{CH}_2\text{SH}$  bond and the fourth again a *gauche* one to the  $\text{CH}_2 - \text{CH}_2\text{CH}_2\text{SH}$  bond.