FOURIER TRANSFORM MICROWAVE SPECTRA OF ISOBUTYL MERCAPTAN

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In order to obtain information on stable conformers and internal motions of isobutyl mercaptan (2-methyl-1-propanethiol), we have analyzed its rotational spectra observed by Fourier transform microwave spectroscopy. We may expect that isobutyl mercaptan exists in five stable rotational isomers, that is, there are two configurations around the $CH(CH_3)_2$ - CH_2SH bond referred to as $gauche$ and $trans$ and more than two minima on the internal rotation of the SH group. We scanned the frequency region from 3.7 to 25 GHz using a sample of isobutyl mercaptan 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: 36 a-type, 28 b-type, and 25 c-type transitions for the G_1 and 36 a-type and 25 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. On the other hand, 25 a-type, 25 b-type, and 16 c-type transitions were assigned 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 demonstrate that there are two minima for the $gauche$ form at the CCSH dihedral angle of 72.2° and 298.1°, which correspond to G_1 and G_2, as observed, whereas two minima at the CCSH dihedral angles of 73.8° and 286.2° are equivalent for the $trans$ form. These $ab\ initio$ results are in good accord with the experimental observations. The rotational spectra of the ^{34}S species were assigned for all the three rotational isomers and the four ^{13}C species for the two $gauche$ forms, all existing in natural abundance. These observations on isotopic species give further support to the above results on the stable rotational isomers.