

CONFORMATIONAL ANALYSIS, BARRIERS TO INTERNAL ROTATION AND AB INITIO CALCULATIONS OF 3-FLUORO-1-BUTENE

SEUNG WON HUR, TODOR K. GOUNEV, GAMIL A. GUIRGIS AND JAMES R. DURIG, *Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-2499.*

The far infrared spectrum of gaseous 3-fluoro-1-butene has been recorded at a resolution of 0.10 cm^{-1} . The asymmetric torsional fundamental of the most stable HE (hydrogen atom eclipses the double bond) and the higher energy FE (fluorine atom eclipses the double bond) conformations have been observed at 88.7 and 105.9 cm^{-1} , respectively, each with excited states falling to lower frequencies. From these data, the asymmetric torsional potential function governing internal rotation about the C-C bond has been determined. The potential coefficients are: $V_1 = -212 \pm 11$, $V_2 = 381 \pm 12$, $V_3 = 576 \pm 6$, $V_1' = 322 \pm 17$, $V_2' = -214 \pm 10$ and $V_3' = -240 \pm 13\text{ cm}^{-1}$. From variable temperature (-55 to -100°C) measurements of the infrared spectra of xenon solutions, the enthalpy difference between the HE and FE conformers has been determined to be $87 \pm 6\text{ cm}^{-1}$ ($250 \pm 17\text{ cal/mol}$). The same determination yields an enthalpy difference of $292 \pm 5\text{ cm}^{-1}$ ($835 \pm 15\text{ cal/mol}$) between the HE and the least stable ME (methyl group eclipses the double bond) conformer. The vibrational data have been compared to the corresponding quantities obtained from ab initio calculations employing the MP2/6-31G(d) basis set.