MICROWAVE SPECTRUM AND AB INITIO CALCULATIONS FOR DIFLUOROSILYL ISOCYANATE, HF_2SiNCO

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The rotational spectrum for the normal isotopologue of difluorosilyl isocyanate, HF_2SiNCO, has been measured in the 5–15 GHz range using a 480 MHz bandwidth chirped-pulse Fourier-transform (CP-FTMW) microwave spectrometer and a Balle-Flygare resonant cavity FT-microwave spectrometer. Clearly resolved nuclear quadrupole hyperfine splittings arising from the ^{14}N nucleus are consistent with the predicted hyperfine patterns, and indicate near-cylindrical symmetry around the nitrogen atom ($\chi_{bb} - \chi_{cc} = -0.0214(58)$ MHz).

Ab initio optimizations at several levels of theory (up to CCSD(T)/6-311++G(3df,3pd)) yielded two energetically very similar structures which differ predominantly in the value of the H–Si–N=C dihedral angle (“cis” $= 0°$ or “trans” $= 180°$). Both structures have rotational constants similar to the observed values ($A = 7111.2810(18)$ MHz, $B = 1565.7758(5)$ MHz and $C = 1347.5228(8)$ MHz), although the experimental constants, particularly A, seem to point to the slightly higher energy “cis” structure as the observed species. However, at every level of theory the difference in energy between the two forms is small (less than 0.45 kJ mol^{-1}) and a variation of the A rotational constant with the chosen level is observed, since this constant is especially sensitive to the Si–N=C angle and Si–N=C=O dihedral. Details of the two possible structures and their stabilities will be presented based on the computational and experimental data, and the results for HF_2SiNCO will be compared to related molecules.