Ph_2

THE GAS PHASE STRUCTURE OF TRIFLUOROETHYLIDYNESULFUR TRIFLUORIDE, CF_3–C≡SF_3

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The gas phase structure of CF_3-C≡SF_3 has been studied by electron diffraction, microwave spectroscopy, vibrational spectroscopy and ab initio methods. Various models have been employed in the electron diffraction analysis: rigid model, non-rigid model with free internal rotation and non-rigid model with large amplitude C-C≡S bending motion. All models result in a bent C-C≡S skeleton with CCS = 155 (3)°. This is a substantially greater deviation from linearity than found in solid CF_3CSF_3 (CCS = 171.5 (2)°). The remaining geometric parameters (r_a values with 3σ uncertainties) are: C≡S = 1.434 (14), C-C = 1.45 (2), C-F = 1.329 (4), S-F = 1.561 (3) Å, FSF = 93.2 (9)° and FCF = 108.4 (5)°. The electron diffraction model is supported by broad band microwave spectroscopy which yields B+C = 1.545 GHz in very good agreement with the structure derived by electron diffraction. The vibrational data (IR gas, IR matrix and Raman liquid) are compatible with a linear or bent skeleton. Ab initio calculations have been performed for HC≡SF_3, FC≡SF_3, CH_3C≡SF_3 and CF_3C≡SF_3. All are linear at carbon using SCF wavefunctions, but are predicted to be bent, though to very different extents, when electron correlation is included at the MP2 level. The result of a bent C-C≡S configuration has been rationalized by a small contribution of the ylidic type resonance structure