HIGH RESOLUTION ROTATIONAL SPECTRA OF THE FCO_2 RADICAL IN ITS X^2B_2 STATE

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The fluoroformyloxyl FCO_2 radical is of atmospheric interest since it may be produced during the stratospheric degradation of HFCs. It is therefore important to characterize this species in order to better understand its atmospheric chemistry. Moreover, FCO_2 should be stable enough in the atmosphere so its abundance may allow its detection by spectroscopic methods [a]. We hence undertook the first high resolution spectroscopic study of FCO_2 in the gas phase.

It was possible to study FCO_2 in the gas phase by thermolysis of bis-(monofluorocarbonyl peroxide) FC(O)OO(O)CF at a temperature of about 600 K. The rotational spectrum was recorded in the 270 - 345 GHz region, at room temperature at a pressure of 4 mTorr. All the transitions were split into four components due to the spin-spin and spin-rotation interaction.

Ab initio calculations performed at the CCSD(T) level of theory with polarised-valence-triplezeta basis set TZ2Pf with correlation of all electrons were used to predict the spectrum. Due to the symmetry of the ^2B state, only transitions with odd K_a were found. All the lines were fitted to an effective Hamiltonian [b] which comprised spin-spin and spin-rotation interactions together with their corresponding centrifugal distortion operators. We used the CALPGM fitting program of Pickett to derive the spectroscopic constants which were all accurately determined up to the quartic centrifugal distortion constants.

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[a] G. A. Argüello, H. Grothe, M. Kronberg, H. Willner and H.-G. Mack *J. Phys. Chem.* **99**, 17525-17531 (1995).

[b] M.Bogey, P. B. Davies, C. Demuynck, J. L. Destombes and T. J. Sears *Mol. Phys.* **67**(5), 1033-1051 (1989).