BOND-STRETCH ISOMERISM IN SFCl AND OTHER SULFUR HALIDES

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We have identified bond-stretch isomers in $^3A''$ excited states of SFCl and other triatomic sulfur halides using high-level *ab initio* techniques [RCCSD(T)/aug-cc-pVQZ]. These bond-stretch isomers are true minima on their potential energy surfaces, and they are manifested by alternation in bond type: There is a shorter (covalent) bond, and longer (recoupled pair) bond in all cases, while the bond angle is nearly constant for the isomers ($\sim$90°). The SFCl isomers are $\sim$15 kcal/mol above a third nearly linear isomer on the PES for which both bonds are recoupled pair bonds. The recoupled pair bond is one in which the p^2 pair of singlet coupled electrons on the sulfur has been decoupled so that one of the electrons is recoupled to form a bond with a halogen and is typically *$\sim$0.3 Å longer than a covalent bond*. The bond-stretch isomers are interesting because the potential in the direction of bond alternation is very flat, and the barrier between the isomers is very low ($<$1.0 kcal/mol for SFCl, for example). Harmonic frequencies of these minima and the transition states between them have been calculated. Potential energy surfaces are being calculated in order to obtain a numerical solution to the nuclear Schrödinger equation.