THEORETICAL STUDIES OF OBSERVABLE TRANSITIONS TO RECOUPLED PAIR BONDED STATES OF SULFUR HALIDE COMPOUNDS: SF/SCl ($X^2\Pi \rightarrow A^2\Sigma^-$), SF_2/SCl_2 ($X^1A_1 \rightarrow 1^1B_1$, $X^1A_1 \rightarrow 1^1A_2$), AND SFCl ($X^1A' \rightarrow A^1A''$)

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In previous studies regarding the nature of hypervalent behavior, we identified low-lying excited states of SF($a^4\Sigma^-$), SCl($a^4\Sigma^-$), SF_2(a^3B_1,b^3A_2), SFCl(a^3A'') and SCl_2(a^3B_1) that involve recoupled pair bonding (rpb), where the electrons of the S $3p^2$ pair are made available to form bonds. While the transitions from the ground states to the quartet states of SF/SCl and the triplet states of SF_2/SFCl/SCl_2 are spin-forbidden, each of these excited states have analogs with formally spin- and dipole-allowed transitions (except $^1A_2$). We performed high level MRCI+Q/aug-cc-pV(Q+d)Z calculations in order to characterize the electronic spectra, spectroscopic constants, and bonding of these species, and made comparisons to available experimental data. We found that excitation into the experimentally known and dipole-forbidden singlet rpb state, SCl_2(B^1A_2), can explain the well-known photodissociation behavior of SCl_2 used to produce SCl($X^2\Pi$) radicals in the laboratory.[a] Finally, we have also found a possible system of bond-stretch isomers on the SFCl(A^1A'') potential energy surface that is analogous to the behavior on the triplet surface reported in our previous study.[b]

[a]Howe, J. D.; Ashfold, M. N. R.; Morgan, R. A.;Western, C. M.; Buma, W. J.; Milan, J. B. and de Lang, C. A. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 773.

[b]Leiding, J.; Woon, D. E., and Dunning, T. H., Jr. *J. Phys. Chem. A* **2011**, *115*, 329.