A NON-EMPIRICAL SCF MO STUDY ON THE FIRST TRIPLET STATE POTENTIAL ENERGY SURFACES AND VIBRATIONAL FREQUENCIES OF SIMPLE THIOCARBONYLS

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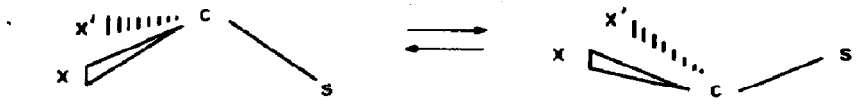
Simple thiocarbonyls are planar in their electronic ground states but, by anology with the corresponding carbonyls, are expected to be non-planar in their S_1 and T_1 states.[1,2] Theoretical studies on the excited states of these molecules are of particular interest, since the calculated potential energy surfaces may aid the interpretation of their highly structured $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$ absorption spectra.

The first triplet state vibrational potentials of small model molecules, containing the thiocarbonyl functional group have been studied with the aid of ab initio MO SCF theory. Large portions of the ground state singlet and first triplet state potential energy surfaces have been calculated and theoretical estimates have been obtained for the excited state vibrational frequencies, using a perturbation theoretical approach.[3] The theoretical results on the triplet state vibrational frequencies show good agreement with the available experimental information obtained from the $T_1 \leftarrow S_0$ absorption spectra. The calculated triplet state double minimum potentials for the



pyramidal inversions have been studied in some detail using an analytic approximation to the ab initio potential. The calculated inversion barrier heights are of the order of ~ 6-8 kcal/mole (for $F_2C=S$, isoelectronic with $Me_2C=S$, a barrier of 7.74 kcal/mole, while for FClC=S, a barrier of 5.80 kcal/mole were obtained). The calculated potential energy surface of the first triplet state of $F_2C=S$ is shown on the figure.

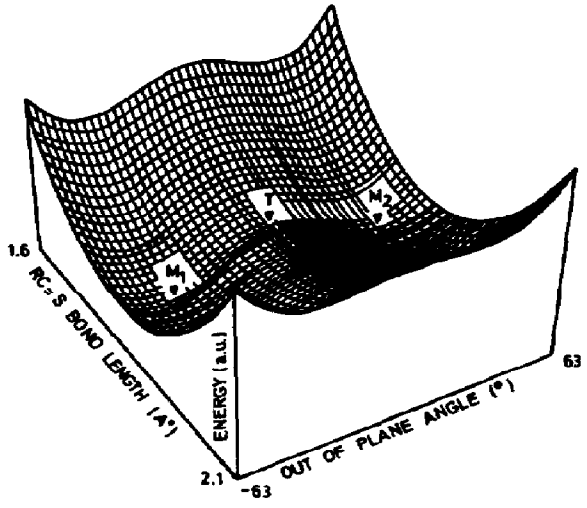


Figure. Energy as a function of the out of plane angle θ and the RC═S bond length in $F_2CS(3_{A_2})$.

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