OPTICAL SPECTROSCOPY AND SECOND EXCITED STATE PHOTOPHYSICS OF SMALL THIOCARBONYLS

R. P. Steer, A. R. Knight and D. J. Clouthier

Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, S7N OWO (Canada)

D. C. Moule

Department of Chemistry, Brock University, St. Catharines, Ontario, L2S 3A1 (Canada)

UV-visible absorption spectra with resolution of ca. 100,000 have been obtained for portions of the $S_2 \rightarrow S_o$ ($\pi^* \leftarrow \pi$) band systems of Cl_2CS and ClFCS in the gas phase at 298 and 196°K. Two excited state frequencies expected to be prominent on Franck-Condon grounds have been identified. Data for the C-S stretching mode follows.

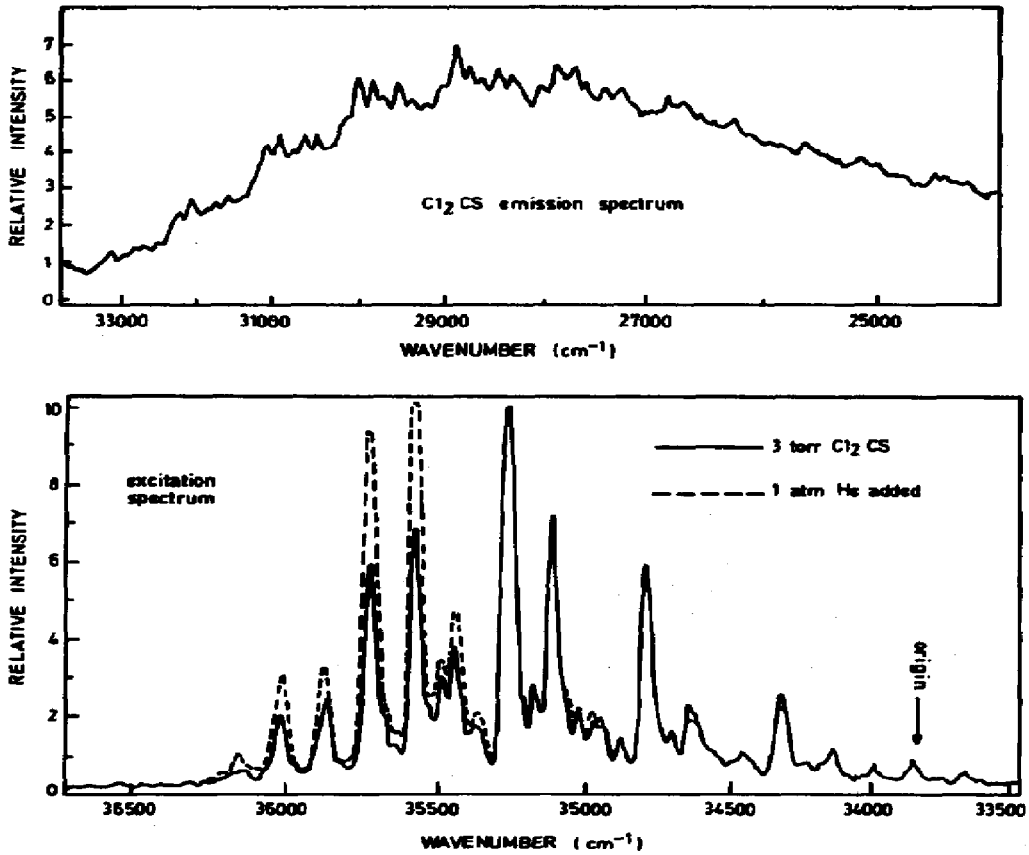
State	approximate C-S bond order	H_2CS	frequency (cm^{-1}) ClFCS	Cl_2CS
$\tilde{X}$	2	1063	1257	1139
$\tilde{A}$	1½	819*	877 or 964	907
$\tilde{B}$	1	433	564	504

*Data of Judge and King, 1977.

For the out-of-plane bending mode in S_2, small inversion doublet splittings ($<1cm^{-1}$) have been observed and inversion barrier heights of $>2000\ cm^{-1}$ have been calculated for both ClFCS and Cl_2CS using the method of Coon et al[1].

Both ClFCS and Cl_2CS exhibit remarkably high quantum yields of "anomalous" $S_2 \rightarrow S_o$ fluorescence in the gas phase at low pressure. Fluorescence quantum yields from single vibronic levels near the origin are unity within experimental error for Cl_2CS and exceed 0.55 for ClFCS. No $S_2 \rightarrow S_o$ fluorescence has been observed for F_2CS, however.

Fluorescence spectra of these compounds are broad and relatively structureless, although a progression of ten members in the C-S stretching mode can be identified in Cl_2CS. Quite well-resolved fluorescence excitation spectra can be obtained, however. Examples of these spectra are shown below:



Analysis of the excitation, fluorescence and absorption spectra, combined with measurements of selected single vibronic level fluorescence quantum yields, temperature and pressure effects, have permitted the location of the $S_2 \leftarrow S_0$ band system origins of these molecules (which lie far to the red of the absorption maxima). Lifetime measurements for selected S_2 single vibronic states reveal non-exponential decays in the low pressure isolated molecule limit. Present data suggest that ClFCS and Cl_2CS in their S_2 states are examples of "intermediate case" molecules.

Population of higher vibrational levels of S_2 permits access to a competing fast radiationless process (likely leading to photodissociation), the onset of which can be determined by the addition of inert thermalizing gases and from the appearance of diffuseness in the absorption spectra.

Reference

1. J.B. Coon, N.W. Naugle and R.D. McKenzie, J. Mol. Spectroscopy, 20, 107 (1966).