The $^1A'' \leftarrow {}^1A'$ Electronic Transition in Thiocarbonyl Chlorofluoride

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Summary The near-u.v. band spectra of ClFCS have been photographed under conditions of high pressure-path and resolution at 30° and −77°.

IN ClFCS vapour a weak absorption extends from 5000 to 3500 Å in a series of well defined bands. Under high resolution the bands display two distinct types of rotational fine structure, the set of bands at shorter wavelengths having a single sharp line-like feature, the set at longer wavelengths possessing a broad intensity maximum followed by what appears to be a band head. From an analogy to the singlet–singlet and singlet–triplet transitions in Cl_2CS [1,2] and F_2CS [3,4] we assign the latter to the spin forbidden $^3A'' \leftarrow {}^1A'$ transition and the former to the $^1A'' \leftarrow {}^1A'$ transition. In the case of F_2CS and Cl_2CS, these transitions have been shown to be accompanied by significant changes in the C=S bond length as well as by a distortion of the structure into a nonplanar form. The barriers to molecular inversion in the $^1A_2$ states of Cl_2CS[2] and F_2CS[3] have been evaluated as 598 cm^{-1} and 3100 cm^{-1}, respectively, which could be taken to be the upper and lower bounds to the barrier height in ClFCS. The i.r. and Raman spectrum of thiocarbonyl chlorofluoride has been obtained recently[5] and a normal-co-ordinate analysis carried out. The ground-state frequencies from this work are listed in Table 1.

Thiocarbonyl chlorofluoride was prepared by the action of SbF_3 on a dilute solution of Cl_2CS in tetrahydrothiophen 1,1-dioxide. It was found that the addition of small amounts of $SbCl_5$ to the mixture, as well as increasing the rate of reaction, improved the overall yield to 40%. The near-u.v. spectrum of the vapour was photographed in the first order of a 20 ft Ebert spectrograph[6] at a resolution of 150,000. Pressure-paths for this experiment ranged from 0·1 to 14 metre-atmospheres. The pressure-path at dry-ice temperatures was limited to 0·6 metre-atmospheres because of the reduced vapour pressure at that temperature.

It was possible to predict the electronic energies of the $^1A''$ and $^3A''$ states of FClCS from a correlation to the spectra of Cl_2CS and F_2CS. If the $^3(\pi^*n)$ and $^1(\pi^*n)$ states of ClFCS are intermediate in energy to the corresponding states of Cl_2CS and F_2CS then from the following electronic origins in cm^{-1}: $^1A_2$, Cl_2CS 18,716·3; $^3A_2$, Cl_2CS 17,492·0; $^1A_2$, F_2CS 23,477·1; $^3A_2$ F_2CS 22,191·1 it follows that the original bands for the $^1A''$ and $^3A''$ ClFCS systems should lie in the region of 21,096 and 19,841 cm^{-1}, respectively. Although interference in the ClFCS spectrum from cold triplet and hot singlet bands is quite severe in the region predicted for the origin, at dry-ice temperatures a band with distinct singlet rotational structure was observed at 21,657·8 cm^{-1}, which could be assigned to the electronic origin. To the blue side of this band a prominent progression in a frequency interval of 408 cm^{-1} was observed. All of these bands acted as sub-origins for hot band progressions extending to longer wavelengths in intervals of 539 cm^{-1}. On Franck–Condon grounds these two progressions were assigned to ν_6' and ν_6'' since a nonplanar distortion of ClFCS during electronic excitation would result in the activity of ν_6, the mode to which aplanar motion most closely corresponds. Frequency intervals of 351 and 582 cm^{-1} were also observed in the spectrum of the vapour at dry-ice temperatures. From a correlation of the ground-state fundamental frequencies listed in Table 1 these intervals are assigned to ν_4' and ν_3'. The ν_3' mode can be described approximately as C–Cl stretching which drops from 612 to 582 cm^{-1} on excitation. This seems to be a general effect for the halogen stretching mode since the corresponding frequencies in Cl_2CS drop on excitation from 504 to 480 cm^{-1}. In F_2CS the drop is from 787 to 736 cm^{-1}. If the absorption process can be considered to result in a carbon centre with greater sp^3 character, the reduction in the ν_3 stretching frequency on electronic excitation would be compatible with the n.q.r. studies on the C–Cl bond strength.[7] Table 2 gives the observed and calculated levels of ν_6' in the $^1A''$ state. A quadratic term perturbed by a Lorentzian barrier term was used to approximate the ν_6' vibrational potential. The best fit to the observed data was obtained from the function $V(Z) = 59{\cdot}29Z^2 + 16200{\cdot}00| (5{\cdot}0 + Z^2)$ where Z is the reduced normal co-ordinate. The potential barrier in $V(Z)$ opposing planarity is calculated to be 1915 ± 25 cm^{-1}. The minimum in $V(Z)$ occurs at $Z = 3{\cdot}2$. The 1915 cm^{-1} barrier is very close to the mean of the 582 cm^{-1} and 3100 cm^{-1} barriers in Cl_2CS and F_2CS which indicates that the forces within the $(n\pi^*)$ excited states of the thiocarbonyl chlorides and fluorides can be transferred from one molecule to another in a way similar to the Urey–Bradley force-field transferability of the ground-state[5] force constants. As yet we have been unable to explain the increase in barrier height with fluorine substitution.

TABLE 1

Vibrational frequencies of ClFCS *in the* ^{1}A′ *and* ^{1}A″ *states in cm*$^{-1}$

	$^1A'$ (ground state)	$^1A''$ (excited state)
$\nu_1(a')$	1257	—
$\nu_2(a')$	1014	—
$\nu_3(a')$	612	582·6
$\nu_4(a')$	427	351·7
$\nu_5(a')$	323	223·4
$\nu_6(a'')$	539	408·4

TABLE 2

Observed and calculated levels of ν_6' *in the* ^{1}A″ *state of thiocarbonyl chlorofluoride*

	Obs.	Calc.
$v=0$	0·0	0·0
1	0·0	0·03
2	408·4	408·41
3	408·7	408·75
4	797·9	807·66
5	801·3	810·66

We thank Dr. G. W. King for the use of his facilities, and the National Research Council for financial support.

(*Received, May* 14*th*, 1970; *Com.* 747.)

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