The $^3A_2$ State of Thiophosgene

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Summary A band at 5621·1 Å in the absorption spectrum of thiophosgene has been shown to be due to a transition originating from the ground vibronic state.

THIOPHOSGENE exhibits an absorption spectrum in the visible region from 6000 Å to lower wavelengths which has been attributed to an $\pi^* \leftarrow n$ transition in the thiocarbonyl group.[1,2] The electronically forbidden $^1A_2 \leftarrow {}^1A_1$ singlet transition with the origin at 5340 Å, has been analysed in detail by Brand *et al.*[3] These authors assigned five out of the six fundamental frequencies in the $^1A_2$ state of $CSCl_2$ and established that the structure was pyramidal with an out-of-plane angle of 32°.

In the region of the thiophosgene singlet origin, a number of bands of somewhat broader contour were observed which did not fit into the singlet band pattern. At pressure-paths ranging up to 6 m-atm., it was possible to identify these bands out to 5953 Å. This system is assigned to the spin-forbidden $^3A_2 \leftarrow {}^1A_1$ transition. A band at 5621·1 Å provided the key to the vibrational analysis. A temperature study showed that the transition responsible for this band originated from the ground vibronic state. Under a resolution of 150,000 the band displayed a 35,37 chlorine isotope effect of 0·65 cm.$^{-1}$ and an inversion doubling splitting of 5·0 cm.$^{-1}$. Thus, it could be assigned to 4_0^2. Most of the triplet bands were fitted into a vibrational scheme involving quanta of ν_1', ν_2', ν_3', and ν_4' which originated from a band at 5716·9 Å which was taken to be the electronic origin. Unlike the singlet spectrum, transitions from ν_3'' and ν_1'', are observed. It was possible to follow the assignment of the triplet system up to 1000 cm.$^{-1}$ to the blue of the origin, after which the more intense singlet system took over. Table 1 gives the vibrational frequencies of thiophosgene in the $^1A_1$ ground state and the $^1A_2$ and $^3A_2$ excited states. Table 2 gives the calculated energy levels for the ν_4' manifold of $^3A_2$ thiophosgene obtained from a quadratic potential perturbed by a Lorentzian barrier term

$$V(Z_4)/\text{cm.}^{-1} = 74{\cdot}83\, Z^2 + (445100{\cdot}0/54{\cdot}2 + Z^2)$$

TABLE 1. *Vibration wavenumbers of thiophosgene (in cm.$^{-1}$)*

	$^1A_1$ (ground state)		$^1A_2$ (excited state)[b]		$^3A_2$ (excited state)		
	$^{35}Cl_2CS$	$^{35}Cl^{37}ClCS$	$^{35}Cl_2CS$	$^{35}Cl^{37}ClCS$	$^{35}Cl_2CS$		$^{35}Cl^{37}ClCS$
$\nu_1(a_1)$	1139·0	1138·8	907·4	906·8		987·8 ?	
$\nu_2(a_1)$	503·5	499·4	480·0	476·7		474·27	
$\nu_3(a_1)$	288·5[a]	285·8[a]	245·0	243·5	247·35		246·70
$\nu_4(b_1)$ $v_4=1$	471·0	470·7	$0{\cdot}4_2$	$0{\cdot}4_3$		0·24	
$v_4=2$	941·9	941·3	279·6	278·4	298·11		297·05
$v_4=3$	1412·7	1411·7	292·5	291·0	302·87		301·91
$v_4=4$	1883·6	1882·1	447·0[c]	445·2[c]	536·07[c]		534·19[c]
$v_4=5$	—	—	586·9	584·3	600·87		598·82
$v_4=6$	—	—	—	—		706·09	
$\nu_5(b_2)$	818		—	—	—		—
$\nu_6(b_2)$	$\approx\nu_3$[a]		—	—	—		—

[a] ν_3 and ν_6 are observed as two separate peaks in the condensed-phase i.r. spectrum of thiophosgene at liquid-nitrogen temperatures at 294 and 305 cm.$^{-1}$, respectively.
[b] Data taken from ref. 3.
[c] Not corrected for Fermi resonance.

A similar potential function was used to describe ν_4' for the $^1A_2$ state.

$$V(Z_4)/\text{cm.}^{-1} = 76{\cdot}18\, Z^2 + (437900{\cdot}0/55{\cdot}0 + Z^2)$$

The potential barriers opposing planarity are calculated to be 598 and 717 cm.$^{-1}$ in the $^1A_2$ and $^3A_2$ states, respectively. Although the differences in the barrier heights between the singlet and the triplet (n,π^*) state is less marked than in the case of formaldehyde,[4] the structural change accompanying the changes in electron spin in thiophosgene is similar.

TABLE 2

Observed and calculated levels of the ν_4 manifold of $^3A_2$ and $^1A_2$ of $CS^{35}Cl_2$ (cm.$^{-1}$)

	$^1A_2$		$^3A_2$	
	Obs.	Calc.	Obs.	Calc.
$v=0$	0·0	0·0	0·0	0·0
$v=1$	0·4	0·42	0·2	0·13
$v=2$	279·6	279·58	298·1	297·60
$v=3$	292·5	293·53	302·9	302·88
$v=4$	447·0	484·96	536·1[a]	530·22
$v=5$	586·9	578·00	600·9	587·53
$v=6$			706·1	747·19

[a] Uncorrected for Fermi resonance.

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