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STRUCTURES AND DECAY DYNAMICS OF THIOCARBONYL EXCITED STATES*

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Summary

Gas phase absorption, emission and emission excitation spectra have provided detailed ground and excited state structural information for several representative small thiocarbonyls. The ground states are planar but the excited states are generally non-planar and may exhibit a large variation in inversion barrier heights and equilibrium out-of-plane angles. The C–S bond is elongated in excited states, by as much as 0.5 Å in the S_2 $^1(\pi,\pi^*)$ states of Cl_2CS and ClFCS. Tetra-atomic thiocarbonyls appear to decay solely by radiative means from bound levels of their S_1 $^1(n,\pi^*)$ states under collision-free conditions; radiative decay of the corresponding T_1 states has not been observed. Excitation to low-lying vibrational levels of the S_2 states of ClFCS and Cl_2CS in the gas phase results in $S_2 \rightarrow S_0$ emission with high quantum yields ($\varphi_f \rightarrow 1.0$). At higher vibrational energies non-radiative decay (probably leading to dissociation) dominates. The observation of intense emission from S_2 has been exploited to probe the mechanisms of the two-photon absorption in gas phase Cl_2CS. Sequential two-photon absorption via T_1

$$S_0 \xrightarrow{h\nu} T_1 \xrightarrow{h\nu} S_2$$

and bimolecular singlet–singlet energy pooling

$$S_1 + S_1 \rightarrow S_2 + S_0^v$$

have been observed.

1. Introduction

Molecules containing the thiocarbonyl functional group have a number of properties which make them attractive candidates for photochemical, photophysical and spectroscopic study [1]. For example, most thiocarbonyls exhibit $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ absorptions in spectral regions coincident with the fundamental tuning curves of dye lasers, and the $S_0 \rightarrow T_1$ absorption system has an oscillator

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strength which is often only a factor of about 10 smaller than that of the corresponding $S_0 \rightarrow S_1$ system, making direct excitation and observation of both the lowest triplet and lowest excited singlet possible. In addition, the rovibronic structure in the spectra of smaller thiocarbonyls in the gas phase is often sufficiently well resolved to permit determination of the molecular constants of their T_1, S_1 and sometimes S_2 and low-lying Rydberg excited states. Of particular importance is the observation of both fluorescence and chemical reaction from the second excited singlet $^1(\pi,\pi^*)$ states of a variety of thiocarbonyls. In particular, the observation of relatively intense $S_2 \rightarrow S_0$ fluorescence has permitted the direct measurement of S_2 intramolecular decay parameters and has revealed the existence of $2S_1 \rightarrow S_2 + S_0$ energy-pooling processes in gas phase Cl_2CS and $S_2 + X \rightarrow SX^{**} \rightarrow S_0 + X + h\nu$ excimer- and exciplex-forming processes in some aromatic thiones in solution.

In this paper we summarize selected molecular properties of thiocarbonyl excited states and discuss their decay dynamics (much of the work is reviewed in ref. 1). Particular emphasis is placed on an examination of the excited states of small thiocarbonyls in the gas phase. The photochemistry of large thiones in solution has been investigated extensively and has been reviewed [2] by de Mayo and coworkers; it will not be discussed in detail here.

2. Experimental details

Spectral data were taken from many sources, particularly those of Moule and Walsh [1, 3]. Emission and emission excitation spectra, emission quantum yields and fluorescence lifetimes were obtained by methods previously described [4 - 6].

3. Results and discussion

Table 1 summarizes a portion of the existing data on thiocarbonyl excited state structures, derived in large measure from absorption spectra. The $S_0 \rightarrow T_1$

TABLE 1

Representative structures of tetra-atomic thiocarbonyl excited states

State	ω_{C-S} (cm^{-1})		r_{C-S} (Å)		ϑ (deg)		b (cm^{-1})	
	H_2CS	Cl_2CS	H_2CS	Cl_2CS	H_2CS	Cl_2CS	H_2CS	Cl_2CS
$\tilde{X}(^1A_1)$	1059.20	1139	1.6108	1.600	0	0	0	0
$\tilde{a}(^3A_2)$	859	987.8	1.683	≈1.68	16	32	13	726
$\tilde{A}(^1A_2)$	820	907	1.701	≈1.71	10	32	18	620
$\tilde{B}(^1A_1)$	433	504	≈2.17	≈2.10-2.20	—	29.5	—	729

ω_{C-S} is the C–S stretching frequency, r_{C-S} is the equilibrium C–S bond length, ϑ is the out-of-plane angle and b is the inversion barrier height.

and $S_0 \rightarrow S_1$ absorption systems in the visible region ($f \sim 10^{-5}$ and $f \sim 10^{-4}$ respectively) involve n $\rightarrow \pi^*$ electron promotions and exhibit clearly resolved vibrational (and rovibrational in the case of H_2CS) structure. The broad $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$) absorption system ($f \sim 0.1$) in the UV exhibits discrete vibrational bands superimposed on an underlying continuum. The origin of this band system lies lower (conceivably much lower for Cl_2CS) than the lowest sulphur Rydberg states.

Two tetra-atomic thiocarbonyls, H_2CS and Cl_2CS, were chosen to illustrate the most pronounced variations in excited state structures: C–S bond elongation and deviation from planarity. Whereas the ground states are planar about the $>$C=S moiety, the excited states are generally non-planar but may exhibit inversion barriers which range from a few reciprocal centimetres in the case of H_2CS (floppy planar) to several thousand reciprocal centimetres in the case of F_2CS (rigidly non-planar). In a series of tetra-atomic thiocarbonyls, inversion barrier heights and equilibrium out-of-plane angles derived from measurements of inversion splittings generally increase with increasing electronegativity of the substituent atoms, in qualitative accord with Walsh's postulate [7].

It is therefore not surprising that the C–S stretching and out-of-plane bending vibrations dominate the absorption, emission and emission excitation spectra. For excitation to the S_2 $^1(\pi,\pi^*)$ states, the C–S stretching frequency is lowered dramatically (concomitant with a decrease in C–S bond order from 2 to 1), progressions in the C–S stretching mode are exceptionally long and the spectra are very broad (with the resulting complication in spectral analysis that the origin band carries only a small fraction of the oscillator strength and is difficult to observe). Both empirical rules (ωr^3 = constant) and Franck–Condon factor calculations [6] place the C–S bond elongation resulting from $\pi \rightarrow \pi^*$ electron promotion at about 0.5 Å, compared with about 0.1 Å for n $\rightarrow \pi^*$ electron promotion.

Partial electronic energy level diagrams for H_2CS and Cl_2CS are shown in Fig. 1. Similar data are also shown for H_2CO for comparison. These data were taken from analyses of both optical and electron energy loss spectra and the assignments are supported in most cases by calculations. Approximate dissociation limits derived from thermochemical calculations are also shown.

The thiocarbonyl S_1 and T_1 vibrationless levels are generally low lying relative to those of the corresponding carbonyls, and their $S_1 - T_1$ energy gaps are smaller, typically 800 - 1800 cm^{-1}. The second excited singlet states of the tetra-atomic thiocarbonyls and of many larger aliphatic and aromatic thiones are of $^1(\pi,\pi^*)$ character ($^1A_1$ in C_{2v} symmetry) and are also low lying [1]. Unlike the aliphatic carbonyls, thiocarbonyl $^1(\pi,\pi^*)$ excited states are unmistakably identifiable on the basis of vibronic selection rules and are located in readily accessible regions of the spectrum. The next highest energy singlets in the aliphatic thiocarbonyls are Rydberg states [8] which appear as moderately strong narrow-band systems in the 180 - 220 nm region. Only one higher triplet state has been observed in the thiocarbonyls [9]: the $^3(\pi,\pi^*)$ state of Cl_2CS with a band maximum at about 25 000 cm^{-1} has been tentatively identified from electron impact energy loss measurements. If we may generalize from this one observation, it

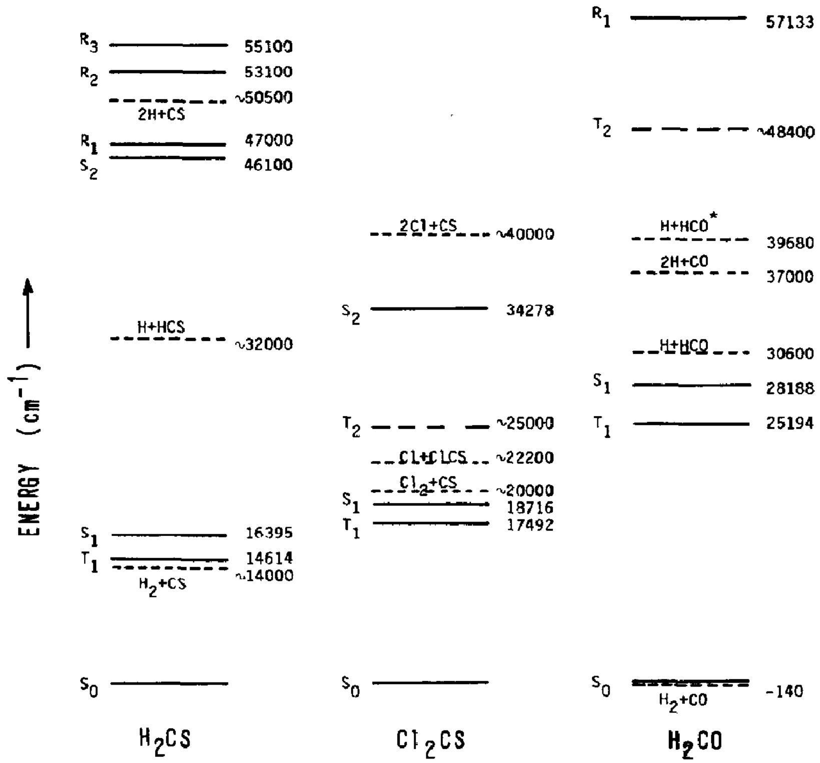

Fig. 1. Electronic energy levels and dissociation limits.

seems probable that the (π,π^*) triplet states of most unconjugated aliphatic thiocarbonyls will lie higher in energy than S_1. The exact locations of the higher triplets and the role which they play in excited state decay remain major uncertainties, however.

The dissociation energies for H_2CS and Cl_2CS shown in Fig. 1 are based on limited thermochemical data [10, 11] and must therefore be considered as only approximate. Nevertheless, both molecular dissociation of X_2CS to ground state X_2 + CS and free-radical dissociation to X + XCS appear to be thermodynamically possible on excitation to S_2 or appropriate vibrationally excited states of S_1 and T_1. In practice, molecular photodissociation has not been observed to date, and available evidence indicates that small thiocarbonyls excited to low-lying S_1 vibronic states under isolated molecule conditions decay exclusively by radiative means. Thus, a value for φ_f of 1.0 has been estimated [12] for isolated Cl_2CS excited to S_1 levels having $E_{\mathrm{vib}} \leqq 3500\ \mathrm{cm}^{-1}$, very well-resolved sharp rotational structure is observed in both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ absorption systems of H_2CS [13] and only resonance fluorescence is observed when Cl_2CS is excited with the 514.5 nm Ar^+ laser line at sufficiently low pressures. The implication is that the molecular dissociation channel, although thermodynamically viable, is inaccessible at visible excitation energies, probably because of the presence of a high activation barrier. (The existence of such a barrier would be consistent with expectations based on H_2CO photodissociation, in view of the difference in stability between CO and CS.) Free-radical dissociation has been observed by Okabe [11] in Cl_2CS at excitation energies well above the S_1 vibrationless level, with a quantum yield of chlorine atoms which increases with decreasing wavelength in the $S_0 \rightarrow S_1$ band system or in the $S_0 \rightarrow S_2$ band system well above the origin. The near coincidence of the onset of this free-radical dissociation channel with the breaking off of $S_1 \rightarrow S_0$ fluorescence as the vibrational energy of S_1 increases [12] places the onset of predissociation about 3650 cm^{-1} above the S_1 vibrationless level in this molecule. No further photochemical studies on small thiocarbonyls in the gas phase have been reported, but present spectroscopic and thermochemical evidence suggests that photodissociation will occur only if several thousand reciprocal centimetres of vibrational energy in S_1 are provided.

The fate of small thiocarbonyls excited to T_1 remains unclear. Emission has not been observed even on direct $S_0 \rightarrow T_1$ excitation; efficient collisional electronic self-quenching appears to be indicated [13]. Larger aromatic thiones in solution, excited initially to S_1, phosphoresce with quantum yields of the order of 0.15 or less. In these molecules S_1 decays almost exclusively by intersystem crossing to T_1; T_1 decays largely by intersystem crossing to S_0 in aprotic solvents and may abstract hydrogen in solvents such as ethanol [1].

$S_2 \rightarrow S_0$ fluorescence has been observed from a wide variety of thiocarbonyls both in the gas phase and in solution [1, 4 - 6]. In the gas phase, fluorescence spectra, quantum yields and lifetimes from the second excited singlet states of Cl_2CS and ClFCS have been recorded as a function of vibrational energy content and pressure. For ClFCS it has been possible to excite singlet vibronic levels of the $\tilde{B}(^1A')$ state from which single exponential decay is observed. The data obtained in these experiments are shown in Table 2. For Cl_2CS single vibronic level excitation has not been possible because of spectral congestion, but quantum yields of fluorescence from low-lying vibrational states are even higher than those of ClFCS and approach unity at excitation energies near the origin. The radiative and non-radiative rate constants determined from short extrapolations of quan-

TABLE 2

Photophysical properties of ClFCS $\tilde{B}(^1A')$

λ (nm)	*Assignment*	τ_f (ns)	φ_f	k_r ($\times 10^6$ s^{-1})	k_{nr} ($\times 10^7$ s^{-1})	k_q ($\times 10^{11}$ l mol^{-1} s^{-1})	σ^2 ($Å^2$)
266.50	1_0^4	17	0.12	7.1	5.2	1.6	24
270.38	$1_0^4 6_1^1$	18	0.24	13.0	4.2	—	—
270.49	1_0^3	28	0.40	14	2.1	1.6	24
267.33	$1_0^3 6_0^2$	14	0.087	6.2	6.5	1.6	24
271.20	$1_0^3 6_1^3$	26	0.22	8.5	3.0	1.2	18
271.36	$1_0^2 6_0^2$	35	0.27	7.7	2.1	—	—
270.10	$1_0^2 4_0^2$	30	0.22	7.3	2.6	—	—
274.08	$1_0^2 4_0^2 6_1^1$	32	0.33	10.3	2.1	—	—
274.45	$1_0^1 3_0^1$ and $1_0^3 6_1^1$	36	0.54	15.0	1.3	1.5	23

tum yield and lifetime measurements to zero pressure are also given in Table 2. Radiative rate constants are of the same order of magnitude as those calculated from oscillator strengths. Non-radiative rate constants generally increase with increasing vibrational energy, as expected.

The most remarkable feature of these data is the smallness of the k_{nr} values obtained on excitation in regions near the $S_0 \rightarrow S_2$ origin. The molecules are only tetra-atomic, but the densities of their S_0, S_1, T_1 and T_2 states in the region of the S_2 vibrationless level are substantial ($\varrho \sim 10^3$ - 10^4 per cm^{-1}) and the $S_2 \rightarrow S_0$ band origin lies well above two dissociation limits, one of which dominates the decay of S_1 at high vibrational energies. Nevertheless, the non-radiative decay rates of ClFCS and Cl_2CS are slow enough that the decay of S_2 near the vibrationless level is dominated by radiative processes. While it would be tempting to ascribe the small non-radiative decay rates solely to factors related to the relatively large S_2–S_1 energy gaps in these molecules, we have been unable to observe $S_2 \rightarrow S_0$ emission ($\varphi_f < 10^{-4}$) from molecules such as F_2CS, Br_2CS, $ClCSOCH_3$ and $CH_3CSC(CH_3)_3$ which have similar energy level spacings and (in the case of the tetra-atomics) similar densities of vibronic states. Although there is some indication that the underlying (dissociative?) continuum in the $S_0 \rightarrow S_2$ absorption system may play a crucial role in determining the non-radiative S_2 decay rates, the mechanism of non-radiative decay of these molecules remains uncertain. Further work is under way.

The observation of S_2 fluorescence from Cl_2CS has been exploited in experiments in which a tightly focused nitrogen-pumped visible dye laser was used to excite emission in the UV–blue [5]. The emission intensity is a linear function of the square of the excitation intensity for optically thin absorbers, proving the two-photon nature of the excitation. Excitation with dye laser fundamentals in the $S_0 \rightarrow S_1$ absorption bands of Cl_2CS results in UV–blue emission whose excitation spectrum is identical with the excitation spectrum obtained in unfocused laser excitation experiments when emission from S_1 in the red is observed, as shown in Fig. 2. Two-photon excitation via real S_1 intermediate states is sug-

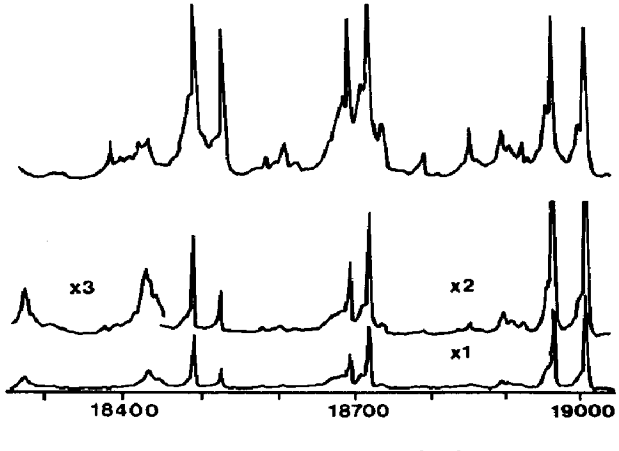

Fig. 2. (a) Two-photon fluorescence excitation spectrum of Cl_2CS (300 nm $< \lambda_{em} <$ 500 nm); (b) $S_1 \leftrightarrow S_0$ one-photon fluorescence excitation spectrum ($\lambda_{em} >$ 600 nm).

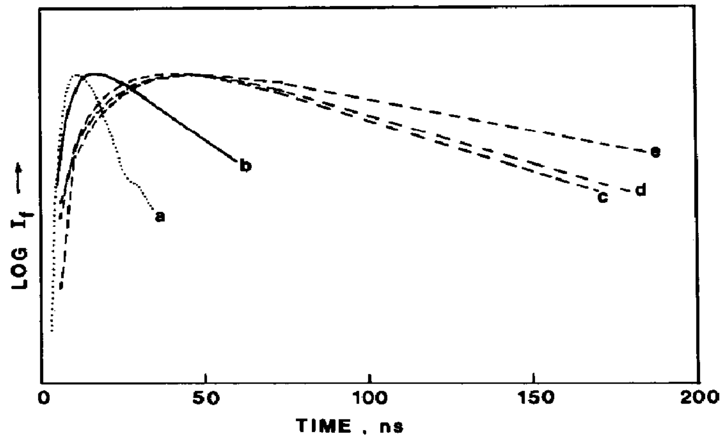

Fig. 3. Temporal profiles ($P(Cl_2CS)$ = 1 Torr): curve a, laser pulse; curve b, λ_{ex} = 578.94 nm, prompt fluorescence; curve c, λ_{ex} = 526.03 nm, delayed fluorescence; curve d, λ_{ex} = 540.75 nm, delayed fluorescence; curve e, λ_{ex} = 534.18 nm, delayed fluorescence.

gested. Excitation with dye laser fundamental wavelengths in the $S_0 \rightarrow T_1$ absorption bands also results in UV–blue emission which exhibits the $S_2 \rightarrow S_0 + h\nu$ spectral distribution. In this case, the excitation spectrum contains many features which are similar to those observed in the $S_0 \rightarrow T_1$ absorption spectrum [15] of Cl_2CS. Two-photon excitation to S_2 via real T_1 intermediate states is suggested in this case. The temporal profiles of the $S_2 \rightarrow S_0$ emissions are entirely different in the two cases, however. When $S_0 \rightarrow T_1$ bands are pumped emission is "prompt" and the decay constants are similar to those obtained when S_2 is pumped directly by one photon in the UV, at similar pressures. In contrast, when $S_0 \rightarrow S_1$ bands are pumped, S_2 emission is delayed and decays over time periods which are many times longer than those of S_2 pumped directly by one-photon absorption. The data are shown in Fig. 3.

The simplest explanation for these observations involves the occurrence of prompt sequential two-photon excitation of S_2 via T_1 in a single laser pulse when the excitation frequency is coincident with $S_0 \rightarrow T_1$ absorption bands, *i.e.*

$$S_0 \xrightarrow{h\nu} T_1 \xrightarrow{h\nu} S_2 \rightarrow S_0 + h\nu_f$$

and bimolecular energy pooling

$$2S_1 \rightarrow S_0^{v} + S_2$$

which generates the observed time delay following excitation in $S_0 \rightarrow S_1$ absorption bands. The energy levels of Cl_2CS are disposed in such a way that prompt emission resulting from two-photon excitation via S_1 is discriminated against since levels in S_2 above the fluorescence threshold would be populated, whereas the ground state product molecule in the energy-pooling process can, and must, carry away a small fraction of the pooled energy so that levels of the electronically excited product molecule which lie below the S_2 fluorescence threshold are populated. A kinetic treatment of a mechanism in which the energy-pooling reaction is the key step reveals that the energy-pooling process proceeds at the gas kinetic rate.

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