The Emission and Absorption Spectra of Chromyl Chloride in an Argon Matrix at 4 K

M. SPOLITI,[1] J. H. THIRTLE, AND T. M. DUNN[2]

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104

The emission and absorption spectra of chromyl chloride (and the pure ^{35}Cl isotopic species) have been obtained in an argon matrix at 4 K. In emission, two systems are obtained and these correlate with the two systems previously found in the absorption spectrum of the pure crystal and which were analyzed as the lowest singlet and triplet systems. The emission systems have, therefore, been assigned as phosphorescence and fluorescence.

INTRODUCTION

Chromyl chloride is a pseudotetrahedral molecule which has an extraordinary electronic spectrum in the visible region, both in the vapor (*1, 2, 3*) and the pure crystal (*4*). The infrared (*5*) and Raman (*6, 7*) spectra have also been reasonably well-defined (Table III) and this combination has afforded an unusual opportunity for a detailed analysis of a pseudotetrahedral molecule since very few cases are known where tetrahedral or pseudotetrahedral molecules have resolvable vibrational and/or rotational structure (*8, 9, 10, 11*) in excited electronic states.

The matrix spectrum was of particular interest for two principle reasons. First, the crystal spectrum exhibits features which were assigned as phonons but could be electronic splittings. Second, it was hoped to obtain the emission spectrum in the matrix in order to verify the nature of the main upper state progression forming vibration in both the vapor (*1, 2, 3*) and crystalline phases (*4*). This verification was desirable because of the previous assignments (*3, 4*) which attributed the upper state progression to a (ν_4) vibration which is almost unchanged ($\sim 4\ cm^{-1}$) in frequency in the ground and excited states, despite its occurrence in the upper state of about 8 quanta and with the intensity maximum at about the fifth quantum.

EXPERIMENTAL

The matrices were laid down directly on to a piece of square section fused silica filled with liquid helium. The chromyl chloride reservoir was maintained at $-80°C$ and the argon pressure regulated so as to maintain a dynamic pressure of 3×10^{-5} Torr in the vacuum space. The matrices were a very light orange in color and ranged in thickness from about 1.5–5 mm.

---

[1] Department of Chemistry, University of Rome, Rome, Italy.
[2] Request for reprints should be addressed to T. M. Dunn.

The emission spectra were obtained by irradiation of the matrix by a 1.5 kw Hg/Xe lamp using water and Corning 3-75 filters. Exposure times were, typically, between 15–30 min. The spectra were all recorded on Kodak 103aF and 103aD film on a Bausch and Lomb 1.5 metre grating spectrograph with a theoretical resolving power of about 35,000.

The $CrO_2{}^{35}Cl_2$ used was prepared from $Na^{35}Cl$ in the conventional way.

RESULTS

The absorption and emission frequencies of the CrO_2Cl_2 species are given in Tables I and II and a microdensitometer trace of the origin region in both absorption and emission is shown in Fig. 1. The Franck–Condon intensity pattern of the absorption spectrum is very similar to both that of the vapor and the crystal, with the intensity maximum occurring in the fourth quantum of the main progression mode. The pattern of the region from the origin to about 300 cm⁻¹ higher frequencies from it is also identical, i.e., the first feature, other than the main progression, occurs about 200 cm⁻¹ from the origin in both the matrix and the crystal spectrum.

DISCUSSION

A comparison of the lowest frequency band of the absorption system with the highest band in the emission system shows a difference of only 70 cm⁻¹ in the sense ν(emission) $> \nu$(absorption). This is attributed to a matrix effect although it must be noted that it is in the opposite sense of that usually observed for the emission absorption difference. The exact nature of this unusual effect is currently under a detailed examination. The first band in each case is therefore, interpreted as the electronic origin and the conclusion to be drawn is that the system onset is electronically allowed. This conclusion is not possible from any analysis of either the vapor or crystal absorption system and is an important one from the point of view of a decisive conclusion regarding the direction of the electronic transition moment in this transition. (The molecular axis convention is as

TABLE I

The Absorption Spectrum of $CrO_2Cl_2{}^{35}$ in an Argon Matrix at 4°K

No	Wavelength (nm in air)	cm⁻¹(vac)	Assignment
1	580.86	17211	0^0 (origin of singlet system)
2	576.04	17355	4^1
3	573.63	17428	7^1
4	571.36	17497	4^2
5	568.92	17572	$4^1 7^1$
6	566.68	17642	4^3
7	564.28	17717	$4^2 7^1$
8	562.19	17783	4^4
9	559.79	17859	$4^3 7^1$
10	557.72	17925	4^5
11	555.33	18002	$4^4 7^1$
12	553.31	18068	4^6
13	550.90	18147	$4^5 7^1$

defined previously (*3, 4*), i.e., the z axis is the twofold rotation axis and the chromium and oxygen atoms lie in the xz plane.)

The matrix origins in absorption (17211 cm^{-1}) and emission (17281 cm^{-1}) bracket the previously assumed origin of the vapor spectrum (17234 cm^{-1}) and its correspondence with the bands found in the pure crystal further confirms the assignment of the origin in the vapor (*3, 4*) as a_4, using the trivial notation introduced by Kronig *et al.* (*1*).

Apart from this result, the most important part of the emission spectrum is that commencing with the band at 16,987 cm^{-1}. This band varies in relative intensity by more than an order of magnitude dependent upon the particular matrix. The reason for this is not known but is thought to depend upon the concentration of the matrix or the rate at which it was laid down. The band in question is separated from the highest frequency band by 294 cm^{-1}, which is not a molecular frequency (see Table III). This displacement corresponds to the displacement of the first strong (singlet) band in the

TABLE II

The Emission Spectrum of CrO_2Cl_2 in an Argon Matrix at 4°K[†]

No.	Wavelength (nm in air)	cm^{-1}	Assignment Fluorescence	Phosphorescence
1	578.49	17281	O_0 (F) (Origin)	
2	583.15	143	4_1	
3	585.14	085	7_1	
4	587.75	009	4_2	
5	588.53	16987		O_0 (P) (Origin)
6	589.24	966	$t^*4_17_1$	
7	589.86	949	4_17_1	
8	592.50	873	4_3	
9	593.45	846		4_1
10	594.21	824	$t^*4_27_1+t^*2_1$	
11	594.50	816	$4_27_1+2_1$	
12	597.37	735	4_4	
13	598.49	704		4_2
14	599.32	681	$4_37_1+2_14_1$	
15	601.52	620	2_17_1	
16	603.58	563		4_3
17	604.19	546	$4_47_1+2_14_2$	
18	605.13	521		2_1
19	606.52	483	$2_14_17_1$	
20	609.13	412	$4_57_1+2_14_3$	
21	610.28	381		$2_14_1 (35,37)$
22	610.44	377		$2_14_1 (35,35)$
23	611.38	352	2_2	
24	613.63	292	1_1	
25	614.30	274	$4_67_1+2_14_4 (+6_1?)$	
26	615.52	242		$2_14_2 (35,37)$
27	615.76	236		$2_14_2 (35,35)$
28	616.62	213	2_24_1	
29	618.87	154	$1_14_1+2_14_5 (+6_14_1?)$	
30	620.87	102		$2_14_3 (35,37)$

TABLE II (cont.)

No.	Wavelength (nm in air)	cm^{-1}	Assignment Fluorescence	Phosphorescence
31	621.19	094	$2_2 4_2$	$2_1 4_3 (35,37)$
32	622.56	058		$2_2 (35,37)$
33	622.81	052		$2_2 (35,35)$
34	624.05	020	$1_1 4_2$	
35	624.71	002	$6_1 4_2 (+2_1 4_6?)$	
36	625.51	15982		1_1
37	626.47	958	$2_2 4_3$	$2_1 4_4 (35,37)$
38	626.68	953		$2_1 4_4 (35,35)$
39	628.03	918		$2_2 (35,37)$
40	628.31	911		$2_2 (35,35)$
41	629.56	890	$1_1 4_3$	
42	630.22	863		$1_1 4_1$
43	631.80	823	$2_2 4_4$	
44	632.25	812		$2_1 4_5 (35,35)$
45	633.63	778		$2_2 4_1 (35,37)$
46	633.96	769		$2_2 4_1 (35,35)$
47	635.76	725		$1_1 4_2 (35,37)$
48	636.00	719		$1_1 4_2 (35,35)$
49	639.26	639		$2_2 4_2 (35,37)$
50	639.70	628		$2_2 4_2 (35,35)$
51	641.44	586		$1_1 4_3 (35,37)$
52	641.74	577		$1_1 4_3 (35,35)$
53	643.50	536		$1_1 2_1$
54	645.52	487		$2_2 4_3 (35,35)$
55	646.75	458		$1_1 4_4 (35,37)$
56	647.25	446		$1_1 4_4 (35,35)$
57	647.66	436	$1_1 2_1 4_3 (35,37)$	
58	648.05	427	$1_1 2_1 4_3 (35,35)$	
59	649.11	402		$1_1 2_1 4_1 (35,37)$
60	649.38	395		$1_1 2_1 4_1 (35,35)$
61	654.83	267		$1_1 2_1 4_2 (35,37)$
62	655.35	255		$1_1 2_1 4_2 (35,35)$

†The best phosphorescence emission was obtained using natural abundance CrO_2Cl_2 so that the isotopic splitting was frequently observed (and can be seen clearly in the emission trace, Figure 1) but the fluorescence was best obtained in the isotopically pure $CrO_2Cl^{35}Cl^{35}$ and the frequencies given are almost entirely for this species. A single frequency for a line in the phosphorescence spectrum indicates that the isotopic splitting was not resolved.

*t Features which appear to be traps were observed in absorption (see text) and two of these appear to be observed in emission.
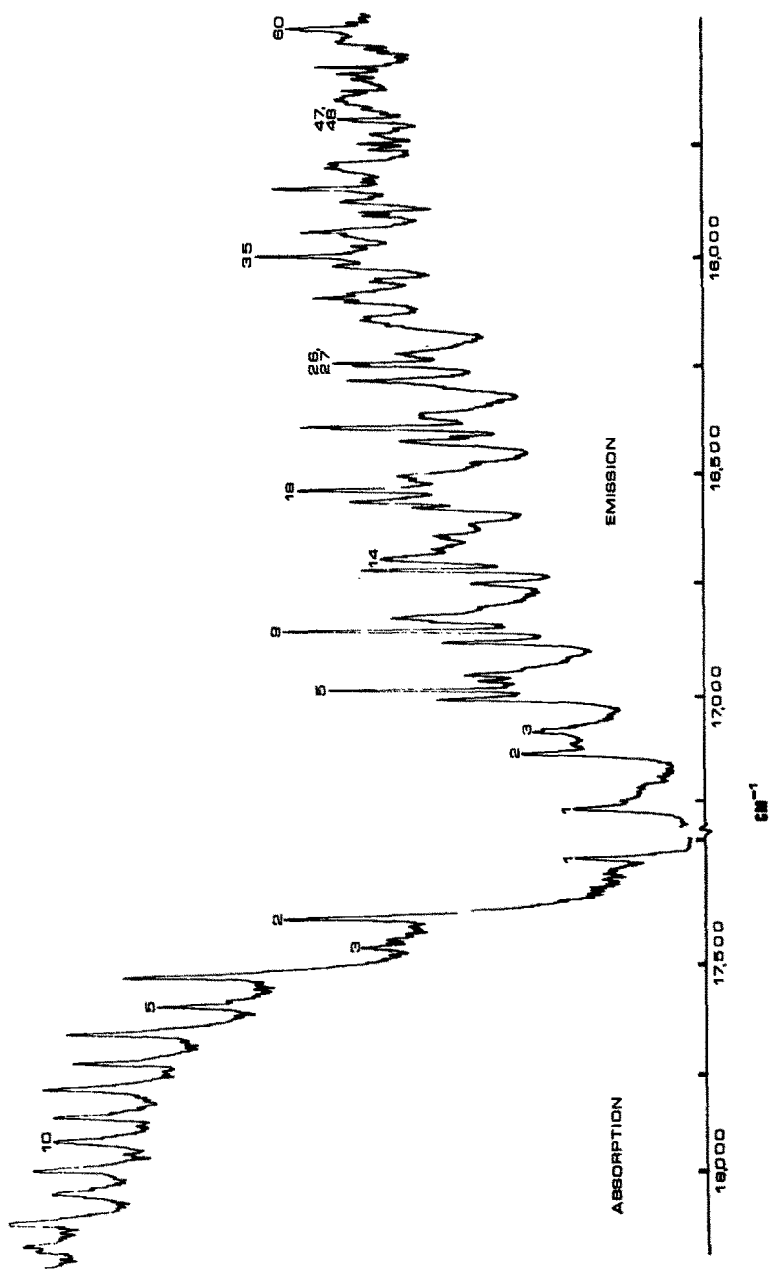
FIG. 1. Absorption and emission spectra of chromyl chloride in an argon matrix at 4 K. The emission spectrum is from natural abundance material while the absorption is of the isotopically pure $CrO_2{}^{36}Cl_2$ species. The band numbers correspond to those given in Tables I and II.

absorption system of the crystal (4) from the origin of the system which was assigned (4) as a triplet transition.

This band is, therefore, assigned as the origin of the "phosphorescence" system of chromyl chloride and its independent character compared with the band system origin about 300 cm⁻¹ to higher frequencies is further confirmed by the simplicity and clarity of the analysis of the bands based upon it as origin. Thus, e.g., the bands 2_1 and 2_2 occur based upon this origin and the isotope effect of this chlorine-stretching mode is clearly visible in the natural isotopic mixture of $CrO_2{}^{35}Cl{}^{37}Cl$ and $CrO_2{}^{35}Cl_2$ both in the fundamentals themselves (by a broadening of band no. 18 which can easily be seen even in the accompanying low dispersion diagram of Fig. 1 by comparing it with e.g., band no. 9, and in the splitting of 6 cm⁻¹ between bands nos. 32 and 33 in Table II.) and in the progressions of ν_4 based upon them—note particularly band nos. 26 and 27.

The other feature of interest is the weak band about 196 cm⁻¹ from the singlet origin in emission, the analog of the band 224 cm⁻¹ from the origin in the crystal absorption system (217 cm⁻¹ in the absorption spectrum of the matrix). The assignment of this vibronic origin seems consistent only with its identification as ν_7 and it is so analyzed in Table II although there is obviously a serious discrepancy between the value of 196 cm⁻¹ and the 215 cm⁻¹ found from the Raman spectrum of the liquid. This frequency is nontotally symmetric and it may well be a matrix effect which is responsible for this difference. No other analysis appears reasonable except to assign it as a completely different electronic state (and there might well be other states lying nearby) but this explanation appears less plausible in the absence of further evidence. Since ν_7 is nontotally symmetric, the vibronic transition moment must be different for these bands, and all totally symmetric progressions based upon them, and this has been confirmed from their analysis in the vapor (3, 4).

It is clear from the spectra, both emission and absorption, that the principal progression forming mode is, indeed ν_4. This near coincidence of the upper and lower state principal progression frequency is one of the main reasons for the complexity of the

TABLE III (4)

NORMAL COORDINATES AND FREQUENCIES OF CrO₂Cl₂

Symmetry (C_{2v})	ν	Activity	Description	Frequency (cm⁻¹)
$A_1(z)$	ν_1		Cr–O str.	995[a]
	ν_2	Raman	Cr–X str.	475[a]
	ν_3	IR	Cr–O scissor	356[a]
	ν_4		Cr–X scissor	140[b]
A_2	ν_5	Raman	O₂–Cl₂ torsion	224[b]
$B_1(x)$	ν_6	Raman	Cr–O str.	1002[a]
	ν_7	IR	CrO₂ rock CrCl₂ "fan"	215[b]
$B_2(y)$	ν_8	Raman	Cr–X str.	500[a]
	ν_9	IR	CrO₂ "fan" CrCl₂ rock	257[b]

[a] Vapor values (see Refs. (3) and (5)).
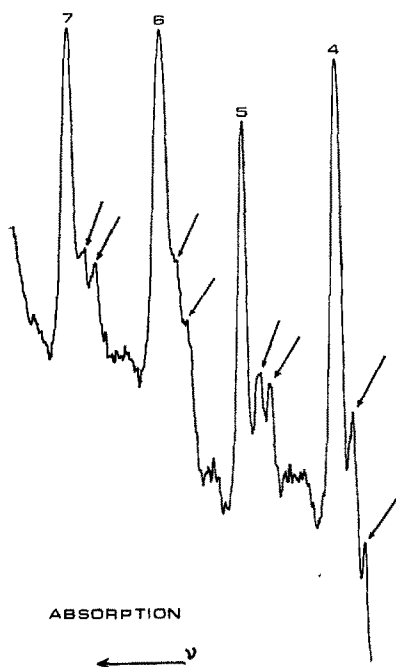[b] Liquid values (see Refs. (6) and (7)).

FIG. 2. Portion of the absorption spectrum of natural abundance CrO_2Cl_2 showing the features analyzed as "traps" (see text). The band numbers correspond with those in Fig. 1.

vapor phase spectrum since, in general, with $kT \sim 200$ cm^{-1}, there will always be a near coincidence between the $4_0{}^m$ band and its $4_1{}^{m+1}$ sequence. This complexity is reduced by the use of pure ^{35}Cl compound but the system is still complex at ambient temperatures, as will be discussed elsewhere (3).

In thick matrices of the natural abundance material, two low intensity satellite bands appear on the low frequency edge of each main progression member being most intense in the $7_1 4_n$ progression members. The appearance of these is illustrated in Fig. 2. They have been analyzed as traps (perhaps differently oriented molecules in the matrix or pairs). These features, at least those based on the $7_1 4_n$ progression, are observed very weakly in emission and have been so assigned (see Table II). There is no doubt, however, that the weak features are not isotopic in character as they can be seen very faintly in spectrum of the isotopically pure $CrO_2{}^{35}Cl_2$.

Finally, it is worth recording one peculiar feature of the emission spectrum. This concerns the role of ν_2 in *both* the fluorescence and phosphorescence systems. The absorption spectrum of vapor crystal and matrix, show no evidence of any intensity enhancement of an upper state progression involving ν_2 and yet this progression appears prominently in the matrix emission spectrum. Even in the gas phase spectrum it is necessary to assign certain bands as having one or two quanta of ν_2 in the ground state (3) but no analogs of these have been found as upper state progressions. It would appear possible that there is an accidental coincidence of the ν_2 progression with the ν_7 progression since this overcomes the obvious objection of the lack of any Fermi diads, but it must be stated that there is absolutely no evidence for this hypothesis. To this extent only, the

spectrum of chromyl chloride requires some further careful vapor phase analysis and this is now under way.

ACKNOWLEDGMENTS

REFERENCES

1. R. DE KRONIG, A. SCHAAFSMA, AND P. K. PEERLKAMP, *Z. Physik. Chem.* **822**, 323 (1933).
2. P. K. PEERLKAMP, *Physica* **1**, 150 (1933).
3. D. S. ALDERICE, T. M. DUNN, AND K. P. LANINI (to be published).
4. T. M. DUNN AND A. H. FRANCIS, *J. Mol. Spectrosc.* **25**, 86 (1968).
5. W. E. HOBBS, *J. Chem. Phys.* **28**, 1220 (1958).
6. H. STAMMREICH, K. KAWAI, AND Y. TAVARES, *Spectrochim. Acta* p. 438 (1959).
7. F. A. MILLER, G. L. CARLSON, AND W. B. WHITE, *Spectrochim. Acta*, p. 709 (1959).
8. S. E. KRASIKOV, A. N. FILIPPOV, AND I. I. CHERNYAEV, *Izv. Sekt. Platiny Drug. Blagor. Metall. Inst. Obshchei Neorg. Khim.* **13**, 19 (1936).
9. B. QVILLER, *Tidsskr. Kjemi Bergv. Metall.* **17**, 127 (1937).
10. A. LANGSETH AND B. QVILLER, *Z. Phys. Chem. B*, **27**, 79 (1934).
11. E. J. WELLS, A. D. JORDAN, D. S. ALDERDICE, AND I. G. ROSS, *Australian J. Chem.* **20**, 2315 (1967).