

The Electronic Absorption Spectrum of Crystalline Chromyl Chloride at 1.7°K

T. M. DUNN AND A. H. FRANCIS

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

The spectrum of chromyl chloride, CrO_2Cl_2 , in the region 6000 Å–3800 Å has been obtained for the crystalline substance at temperatures down to 1.7°K. Three absorption systems have been observed, together with the start of a fourth system at $\lambda < 3800$ Å. One of the systems has been analyzed in some detail and shown to be in agreement with conclusions drawn from the spectrum of the vapor.

INTRODUCTION

The spectrum of chromyl chloride in the vapor phase has been the subject of several previous investigations from 1926 to recent times (1-6) but, so far, the longest wavelength absorption system which extends from ~ 6200 Å–5000 Å in the vapor and in solution (see Fig. 1), has not been analyzed completely, either vibrationally or rotationally. From the vibrational analysis point of view, the main problem has been to assign the origin of the system—and this has not proved to be easy.

In the main, the system consists of, what appears to be, a very long progression, labelled a_i by Kronig *et al.* (3) ($i = -4 \rightarrow 12$), of a single vibration having a frequency of 136–137 cm^{-1} in the excited state. The progression has been followed by previous workers (5, 6) up to ~ 10 quanta, the remarkable fact being that even over this long progression, there appears to be only a slight change of frequency from 137 cm^{-1} to 136 cm^{-1} , a seemingly impossibly small anharmonicity. It is not possible to obtain exact values, however, because of the weakness of the bands at the longest wavelengths and the effects of the chlorine isotopes. This latter problem has made it difficult to compare ground and excited state intervals with complete assurance and so some error may exist in the limits given above. It has also proved (4, 6) difficult, if not almost impossible, to carry out temperature dependence studies on the vapor because of the presence of many low frequency vibrations in this molecule (thus, e.g., even at 77°K only $\sim 88\%$ of the molecules are in their vibrationless ground state) and the vapor pressure (7) is only 10^{-2} torr at -80°C . Because of the difficulties of assigning the origin of the vapor spectrum, it is necessary to use low temperature methods

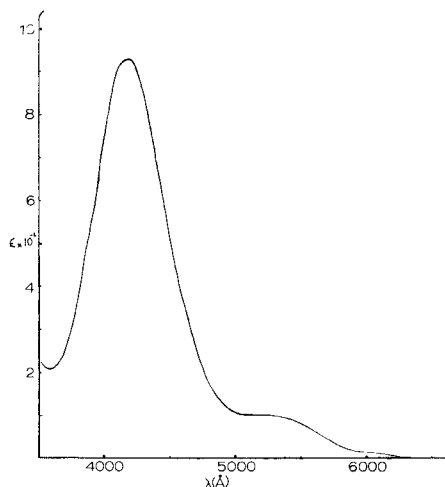


Fig. 1. Spectrum of chromyl chloride in carbon tetrachloride solution at room temperature.

to eliminate those vibrational levels of the ground electronic state which are occupied at room temperature, hence greatly simplifying the spectrum, and it was primarily for this reason that the present work has been done. There has been one previous investigation of the spectrum of solid CrO_2Cl_2 at 20°K (8), but the very limited extent of the spectrum observed led to conclusions which are completely refuted by the present work.

EXPERIMENTAL

The spectra of single crystals of chromyl chloride at 4.2°K and 1.7°K have been obtained. The crystals used ranged in thickness from about 0.1 mm to ~ 2 mm, and were obtained by freezing the purified liquid chromyl chloride between flat fused silica plates. The crystals so obtained were uniform under the polarizing microscope although there was no detectable dichroism.

The low temperatures were obtained by direct immersion of the sample in liquid helium, the lower temperature being achieved by pumping on the helium reservoir until the λ point at 2.17°K had been surpassed. Pressure measurements indicated a low temperature of $\sim 1.7^\circ\text{K}$ at least. No differences were observed between the spectra at 4.2°K and 1.7°K .

Both spectrographic and spectrophotometric methods have been used (1.5-meter Bausch and Lomb spectrograph and a Cary 14 spectrophotometer), because of the particular properties of the systems under study, i.e., a large and rapid intensity change from band to band. The resolving power used was $\sim 35\,000$ for the spectrographic instrument, and the usual ~ 5000 for the spectrophotom-

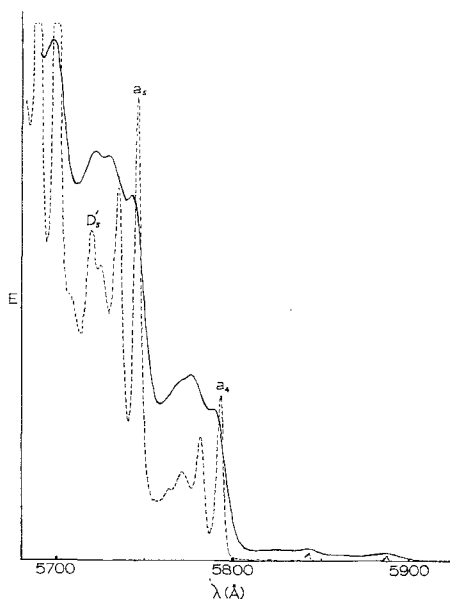


FIG. 2. Spectrophotometric traces of the onset region of crystalline chromyl chloride at 1.7°K. The curve shows the spectrum as recorded using a wide slit width with the lowest dynode voltage setting of the Cary 14 spectrophotometer, whereas the dashed spectrum shows the same crystal scanned with a slit width one-sixth of that used for the previous trace.

eter. The use of the former instrument was necessitated by the very fine absorption lines in the spectrum, which the spectrophotometer did not record faithfully, even at the extreme of its resolving power. Figure 2 shows a portion of the spectrophotometric spectra, there being a difference of a factor of six in the slit width used to obtain the spectra shown there. Figure 2 shows all too clearly the inherent dangers of using spectrophotometers of low resolving power to record low temperature or gas phase absorption spectra where the individual features may be very sharp indeed. Such problems are well recognized in the field of infrared spectroscopy but are infrequently seen, or remarked upon, in the visible and ultra-violet region. It seemed to us to be pertinent to draw attention to this clearly dramatic effect.

RESULTS

The spectra obtained by spectrophotometric means are given in Figs. 3 and 4. The former shows the onset region of the spectrum and the latter shows the spectrum as a whole.

As can be seen from the spectra, the system consists of a low intensity onset of two weak bands followed by an increasingly intense progression of bands spaced

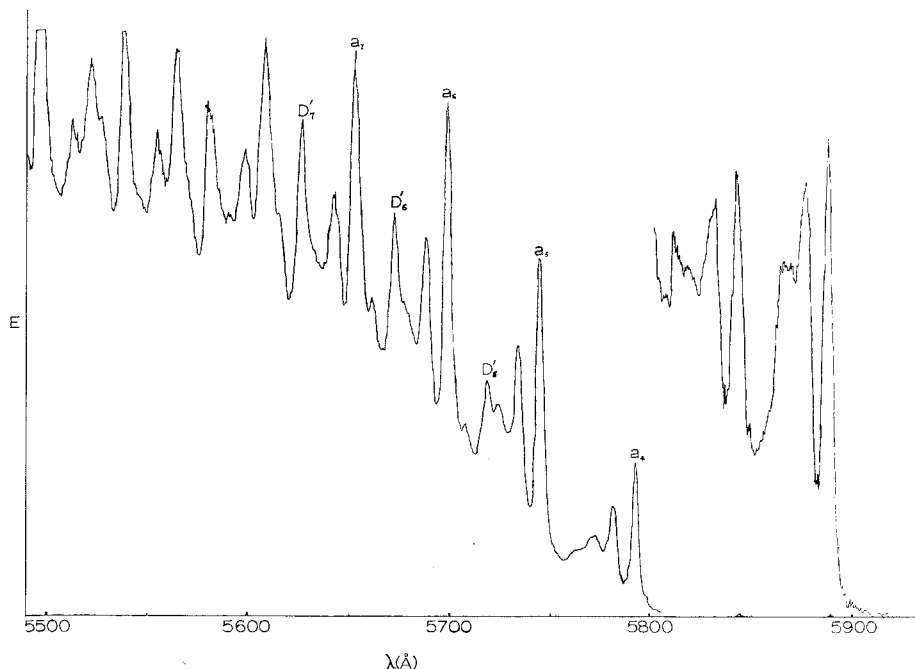


FIG. 3. The spectrum of crystalline chromyl chloride at 1.7°K. The low frequency part of this trace was obtained from a crystal about 2 mm thick whereas the rest of the trace was obtained with a crystal about $\frac{1}{10}$ of a millimeter thick.

at $\sim 140 \text{ cm}^{-1}$. Further to shorter wavelengths, there appears to be a change in the characteristics of the system or else another transition of comparable intensity rises out of the end of the main transition at 4400 \AA . As will be seen from Fig. 1, there is no sign of this in the solution spectrum since the strong transition with its maximum at $\sim 4150 \text{ \AA}$ covers the region completely.

Spectrophotometric studies show that the difference in intensity between the first two weak members of the spectrum—i.e., those at $\sim 5890 \text{ \AA}$ and 5843 \AA —and the first stronger member at 5796 \AA , is at least a factor of 16 and perhaps a little more. It was not possible to get a completely accurate estimate because even at the narrowest slit widths obtainable on the spectrophotometer, the ratios of the intensities of the bands among themselves were still increasing in favor of the band at 5796 \AA , thus indicating that a complete resolution had not yet been obtained. The two weaker bands are almost exactly equal in intensity to each other and their pattern—which is shown in a section of Fig. 3—is exactly the same as for the two first members of the stronger absorption, i.e., at 5796 and 5747 \AA .

In the stronger system, the intensity rises quickly, with a factor of three between the 5747-\AA and 5796-\AA bands and a factor of unity between successive

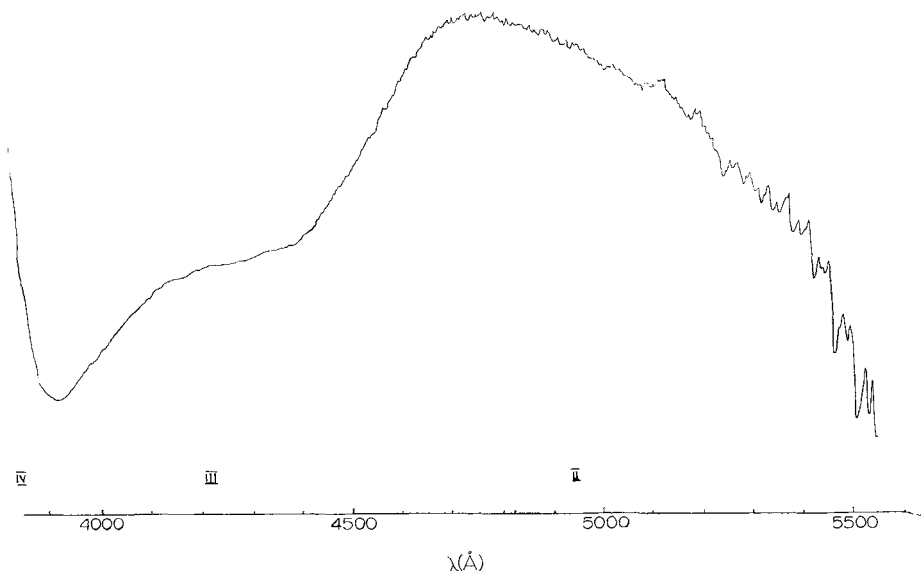


FIG. 4. A very low resolution trace of the whole spectrum of crystalline chromyl chloride down to 3900 Å. This trace does not show the very large number of bands which are present in the region since it was obtained at very wide slit widths. The structure present, however, is real but of low contrast and can be verified in any particular region by using a crystal of the correct thickness. The actual frequencies of the bands are given in Table I.

bands five quanta later. Both the weak and the stronger systems show a further "origin" of intensity at an interval of 224 cm^{-1} from their lowest frequency bands and, in the case of the stronger system, upon this origin is then superposed successive quanta of the 140-cm^{-1} frequency, reaching a maximum after five or six quanta and disappearing after eight.

In the stronger system also, a band appears at $\sim 5470\text{ Å}$ which acts as an origin for further quanta of the 140-cm^{-1} vibration. It attains a maximum after seven quanta then becoming indistinguishable from the background absorption. Despite a careful search, no other definite origins were found although, as Table I shows, it seems likely that there are at least two others. Thus the spectrum of the stronger system is based upon two main origins, each of which is then supplemented by large numbers of quanta of the 140-cm^{-1} vibration and a lower number of quanta of a vibration with a frequency $\sim 1000\text{ cm}^{-1}$. A complete list of band frequencies ($\bar{\nu}_{\text{vac}}$) and wavelengths is given in Table I.

DISCUSSION

The convention used for describing the molecule in the C_{2v} point group is the same as has been used by all the previous workers who carried out the infrared and Raman analysis of the ground state (9-11) and by Helmholz, Brennan, and

TABLE I

System I.

No.	Wavelength (\AA)	Frequency $\nu_{\text{vac.}}$ (cm^{-1})	Assignment*	Trivial Notation
1.	5891.3	16970	ν_{OO^-} origin	
2.	5879.8	17003	p^1	
3.	5869.7	17032	p^2	
4.	5845.3	17103	4^1	
5.	5834	17136	4^1p^1	
6.	5824	17166	4^1p^2	
7.	5815	17192	7^1	

System II.

1.	5796	17248	ν_{OO^-} origin	a_4
2.	5785	17281	p^1	
3.	5775	17311	p^2	
4.	5748	17393	4^1	a_5
5.	5737	17426	4^1p^1	
6.	5727	17456	4^1p^2	
7.	5722	17472	7^1	D_5^1
8.	5711	17505	7^1p^1	
9.	5701	17536	4^2	a_6
10.	5691	17567	4^2p^1	
11.	5682	17595	4^2p^2	
12.	5675	17616	4^17^1	D_6^1
13.	5564	17650	$4^17^1p^1$	
14.	5655	17679	4^3	a_7
15.	5645	17710	4^3p^1	

Wolfsberg (12), who carried out an MO calculation on the energy levels of CrO_2Cl_2 . Thus, the z axis is the twofold axis and the chromium and oxygen atoms lie in the xz plane, etc. We have followed this convention. The complete list of ground-state vibrations and their designations is given in Table II.

The spectrum as a whole is considered to consist of three separate systems I,

TABLE 1
System II. (cont.)

No.	Wavelength (\AA)	Frequency ν_{vac} (cm^{-1})	Assignment*	Trivial Notation
16.	5636	17738	4^3P^2	
17.	5629	17760	4^27^1	D'_7
18.	5617	17798	$4^27^1P^1$	
19.	5610	17820	4^4	a_8
20.	5600	17852	4^4P^1	
21.	5583	17907	4^37^1	D'_8
22.	5571	17945	$4^37^1P^1$	
23.	5566	17961	4^5	a_9
24.	5556	17994	4^5P^1	
25.	5540	18046	4^47^1	D'_9
26.	5528	18085	$4^47^1P^1$	
27.	5523	18101	4^6	a_{10}
28.	5514	18131	4^6P^1	
29.	5497	18187	4^57^1	D'_{10}
30.	5487	18220	$4^57^1P^1$	
31.	5479	18246	4^7	a_{11}
32.	5472	18270	1^1	
33.	5455	18327	4^67^1	D'_{11}
34.	5445	18360	$4^67^1P^1$	
35.	5436	18391	4^8	a_{12}
36.	5430	18411	1^14^1	
37.	5419	18448	$1^14^1P^1$	
38.	5413	18469	4^77^1	D'_{12}
39.	5403	18503	$1^17^1? + 4^77^1P^1$	

II, and III. System I consists of the seven weak bands on the low frequency onset of the spectrum, together with any other bands of similar intensity which might be under the stronger system commencing at 5796 \AA (II). The final system III is the one which has its onset $\sim 4400 \text{ \AA}$ and which continues without very much structure, down to $\sim 3900 \text{ \AA}$. There is no single compulsive argument for sepa-

TABLE 1
 System II. (cont.)

No.	Wavelength \AA	Frequency ν_{max} (cm^{-1})	Assignment*	Trivial Notation
40.	5389	18551	$1^1_4 2$	
41.	5372	18610	$4^3_7 1$	D'_{13}
42.	5363	18641	$1^1_4 1^1_7 1$?	
43.	5355	18669		
44.	5348	18693	$1^1_4 3$	
45.	5332	18749	$4^9_7 1$	D'_{14}
46.	5323	18781	$1^1_4 2^2_7 1$	
47.	5310	18827	$1^1_4 4$	
48.	5300	18863	$1^1_4 4^1_p 1$	
49.	5294	18884	$4^{10}_7 1$	D'_{15}
50.	5284	18920	$1^1_4 3^1_7 1$?	
51.	5270	18970	$1^1_4 5$	
52.	5260	19006	$1^1_4 5^1_p 1$	
53.	5232	19108	$1^1_4 6$	
54.	5221	19148	$1^1_4 6^1_p 1$	
55.	5195	19244	$1^1_4 7$	
56.	5183	19288	1^2 ?	
57.	5171	19333		
58.	5158	19382	$1^1_4 8$	
59.	5146	19427	$1^2_4 1$?	
60.	5135	19469		
61.	5122	19518	$1^1_4 9$	
62.	5110	19564	$1^2_4 2$?	
63.	5085	19660	$1^1_4 10$	

rating this system from II, except that it would be difficult to understand the intensity distribution on Franck-Condon grounds. In a molecule such as CrO_2Cl_2 , where the highest frequency vibration is the $1000\text{-cm}^{-1} \nu_6$, it is difficult to explain an intensity "gap" of a magnitude such as is observed between these two "systems," and a separate classification is, therefore, preferable.

Little can be said about an exact assignment for either systems I or III since

TABLE 1
System II. (cont.)

No.	Wavelength λ	Frequency ν_{osc} (cm^{-1})	Assignment*	Trivial Notation
64.	5065	19738	$X^y_4^n$	
65.	5050	19796	$1^1_4^{11}$	
66.	5027	19887	$X^y_4^{n+1}$	
67.	5014	19937	$1^1_4^{12}$	
68.	4993	20022	$X^y_4^{n+2}$	
69.	4979	20079	$1^1_4^{13}$	
70.	4960	20156	$X^y_4^{n+3}$	
71.	4944	20221	$1^1_4^{14}$	
72.	4925	20299	$X^y_4^{n+4}$	
73.	4908	20369	$1^1_4^{15}$	
74.	4892	20436	$X^y_4^{n+5}$	
75.	4875	20507	$1^1_4^{16}$	
76.	4857	20575	$X^y_4^{n+6}$	
77.	4842	20647	$1^1_4^{17}$	
78.	4825	20720	$X^y_4^{n+7}$	
79.	4792	20862	4^{n+8}	
80.	4777	20928		

*The ground state zero has been omitted in all cases, ie P^1_0 etc.

has been written simply as P^1 , where P signifies a band of phonon type.

neither have been seen in the vapor in the form in which they appear in the crystal spectrum. System I has its origin band (whether electronic or vibronic cannot be decided) at 5891.3 \AA ($16\,919.5 \text{ cm}^{-1}$) and the second member follows with essentially the same intensity and over-all appearance, at a distance of 133.5 cm^{-1} to higher frequencies (see Fig. 3). The progression frequency is

TABLE II
 NORMAL COORDINATES AND FREQUENCIES OF CrO_2Cl_2

Symmetry (C_{2v})	ν_i	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	$\text{O}_2\text{—Cl}_2$ torsion	224 ^b
$B_1(x)$	ν_6	Raman	Cr—O str.	1002 ^a
	ν_7	IR	CrO_2 rock CrCl ₂ "fan"	215 ^b
	ν_8	Raman	Cr—X str.	500 ^a
$B_2(y)$	ν_9	IR	CrO_2 "fan" CrCl ₂ rock	257 ^b

^a Vapor values (see References 6 and 9).

^b Liquid values (see References 10 and 11).

markedly lower than for system II, where it is $\sim 145 \text{ cm}^{-1}$ for the early members, but the crystal frequencies of 33 and 60 cm^{-1} are clearly discernible as well as a second origin (i.e., band 7 of system I) $\sim 222 \text{ cm}^{-1}$ to higher frequencies of the origin. Both these intervals are also a feature of system II and will be discussed below. The third member of the progression should occur on the edge of the onset of the origin of system II and its presence can be divined in several of the microphotometer records.

It is tempting to assign system I as the triplet analog of system II, but this would be precipitous in view of the lack of evidence and when the theoretical aspects of these systems are taken into consideration. If the molecule in question were perfectly tetrahedral e.g., MnO_4^- or CrO_4^{2-} ion, it would appear to be reasonably well established that the transition at longest wavelegnth is, configurationally, $e(d\pi^*) \leftarrow t_1(n)$, i.e., a transition of an electron, which is *completely* (in the absence of f orbital participation) localized on the oxygen atoms, to the completely empty $d\pi^*$, essentially central metal, orbital.

However, in the case of CrO_2Cl_2 , the molecule is not tetrahedral and, in the framework of the coordinates and irreducible representations defined above, the t_1 degenerate lone orbital splits to give three nondegenerate orbitals of types a_2 , b_1 , and b_2 while the $e(d\pi^*)$ orbital yields an a_1 and an a_2 orbital. Thus, the possibility arises of six transitions, all of which are nondegenerate, compared with the two degenerate transitions of the perfectly tetrahedral molecule. (Only one is allowed for electric dipole radiation.) One further piece of evidence comes from the

fact that in CrO_2F_2 (5), the transition equivalent to II occurs at almost the same energy and so it is possible to infer from this that the transition II, at least is concerned with the oxygen atom electrons more than the halogen. Needless perhaps to say, there is no complete separation of these levels into purely oxygen and halogen but it would appear that the coefficients of the highest lying non-bonding orbital are much larger on the oxygen atoms than on the halogen.

The t_1 level, as previously noted, yields only a_2 , b_1 , and b_2 levels so that if further theoretical progress is desired a decision must be made as to the relative order of these orbitals. This is something which is very difficult to predict *a priori*. It is quite clear, however, that six transitions might be expected to result from the removal of the complete degeneracy of the perfect T_d point group molecule, and allowing only electric dipole transitions reduces this to five, $1 \times A_1$, $2 \times B_1$, and $2 \times B_2$.

For these reasons it is not possible, at present, to give a definite assignment to system I, even though on intensity grounds (the ϵ_{max} is only $\sim 1-2$) it might reasonably be assigned as a triplet transition. This tentative assignment is further strengthened by the similarity of the vibrational structure between systems I and II. (Note that this statement has significance only when the $\pi^* \leftarrow n$ character is taken into account.)

System II can be much more thoroughly analyzed since it can be seen in both the crystal and vapor phases and both show well-developed vibrational progressions. The spectrum of the vapor shows (2-6) a long progression of a vibration with a frequency of $135-136 \text{ cm}^{-1}$ and the first strong band in the crystal spectrum at $17\ 248.2$ coincides, within reason, with the band a_4 of the vapor (the two heads of the band assigned to the 35-35 isotope in the vapor, i.e., the strongest heads, occur at $17\ 234.1$ and $17\ 236.9 \text{ cm}^{-1}$) and this is assigned as the 0, 0 band of the system running from this frequency up to about $22\ 000 \text{ cm}^{-1}$. This assignment will be discussed in greater detail elsewhere (6) for the case of the vapor phase—as also will a number of other aspects of the vapor phase spectrum. The “satellite” bands which accompany each of the main bands in this system at a distance of ~ 33 and $\sim 60 \text{ cm}^{-1}$ on the high frequency side, are assigned as lattice modes. They are present throughout the entire spectrum, as far as can be seen, and there is no molecular vibration which could reasonably be assigned as being associated with such a low frequency—particularly in the solid state where there must be additional restrictions on the motions of, e.g., torsion modes such as ν_5 . Warming up the crystal to $\sim 40^\circ\text{K}$ shows quite clearly the presence of a “hot” band 35 cm^{-1} or so on the low frequency side of each main band of the spectrum, and these can be safely assigned as 0, 1 bands of the phonon mode which appears as a 1, 0 band on the high frequency side.

In the crystal, three, and possibly four, origins have been located, two of them with certainty and the other two with some room for error concerning their precise location. The main progression in the system, which is present based upon all

three origins, has a spacing of from $\sim 145 \text{ cm}^{-1}$ down to $\sim 140 \text{ cm}^{-1}$ over the space of seven or eight quanta and it usually reaches its intensity maximum after about 5 quanta. The vibration involved in this progression is assigned as ν_4' , i.e., the CrCl_2 "scissoring" mode which also has a ground-state frequency close to 140 cm^{-1} . It is the only vibration seen in large numbers of quanta (see below), although at least one other frequency $\sim 1000 \text{ cm}^{-1}$ must occur to three quanta or so in order to account for the character of the absorption envelope but the individual quanta are not easy to identify.

The second origin at 5719.5 \AA ($17\,479 \text{ cm}^{-1}$) is assigned as one quantum of ν_7' based on the system origin at 5796 \AA ($17\,248 \text{ cm}^{-1}$). ν_7'' has been found to have a frequency of 211 cm^{-1} by Miller *et al.* (9) and 216 cm^{-1} by Stammreich *et al.* (8)—both in the liquid phase—and there is no experimental value known for the gas phase. The ν_7' value of 224 cm^{-1} shows a slight increase over the ground-state value and this assignment is corroborated by the contour of the analogous band in the vapor phase (6), where the progression of ν_4 based on it, is designated D_4' . The assignment of this band as one quantum of a nontotally symmetric vibration superposed on the origin is also supported by the fact that two quanta of the vibration are never seen—neither in the crystal nor in the vapor—and its band contour in the vapor is completely different from that of the bands based upon the origin at 5796 \AA .

The evidence from the vapor spectrum supports (6) the assignment of the transition as ${}^1A \leftarrow {}^1A$, i.e., it should consist of *B*-type bands, whereas the vapor spectrum clearly shows (6) that bands which are the equivalent of those based upon the origin plus one quantum of the 224-cm^{-1} mode are *C*-type, i.e., ${}^{ev}B_1 \leftarrow {}^{ev}A_1$, so that the assignment of the origin as ν_0^1 is supported by the vapor data. (In the vapor it is impossible to be sure that the equivalent bands really arise from the vibrationless ground state and this is proven conclusively by the present low temperature work.)

The third origin is assigned as the band at 5472 \AA ($18\,270 \text{ cm}^{-1}$). There is some degree of uncertainty with regard to this assignment, for the following reasons. In the crystal, the mode of frequency 33 cm^{-1} associated with the band a_{11} falls exactly at this wavelength so that it is not possible to separate the two bands. It is clear from the rapid increase of intensity of the bands at 5472 \AA , 5430 \AA , 5389 \AA , 5348 \AA , etc. that a progression of the 140-cm^{-1} mode is superposed on a new origin and that this progression leads, on the low frequency side, to the band at 5472 \AA as the first discernible member. Because of the nature of the Franck-Condon envelope of this progression it is possible that the origin is really one quantum of the 140-cm^{-1} mode to still lower frequencies, i.e., where it coincides with the crystal mode associated with a_{10} .

Thus this origin is either 882 or 1022 cm^{-1} from the system origin at $17\,248 \text{ cm}^{-1}$, dependent upon which frequency is actually taken. At this time the higher value of $18\,270 \text{ cm}^{-1}$ (5472 \AA) as the origin is preferred, mainly because neither

of the other vibrations observed changes very much in frequency—except possibly for small increases—so that the interval of 1022 cm^{-1} is taken as representing the upper-state value of the vibration responsible for this origin.

The vibration is assigned as ν_1 , i.e., Cr—O stretching mode, and its frequency of 1022 cm^{-1} suggests a shortening of the Cr—O distance. Although it is not possible to make an assignment with certainty, it seems very likely that the Franck-Condon maximum of the system II at $\sim 4700\text{ \AA}$ is attained mainly by quanta of ν_1' together with quanta of ν_4' . In fact, it is possible to trace the $1_0^1 4_0^n$ progression right to the maximum of system II, at which stage, $n = 17$. The successive band separations are remarkably regular as perusal of Table I shows. It would be impossible to claim that some other coincidence has not led to the occurrence of a still further progression which takes over smoothly from the $1_0^1 4_0^n$ progression, but there is no abrupt change which could be attributed to this. For this reason the assignment has been made as shown in Table I. There is also a possibility that this origin represents a quantum of ν_6' based on the low frequency origin, i.e., the antisymmetric Cr—O stretching mode—and this alternative will be discussed further elsewhere (6).

The progression which accompanies the previous one right to the intensity maximum of the system starts in the region of 5065 \AA ($19\,738\text{ cm}^{-1}$), i.e., 2490 cm^{-1} from ν_{00} . No assignment has been made for it and it appears simply as $X_0^y 4_0^n$ in Table I. It most likely consists of two quanta of ν_1' or perhaps ν_6' but the remaining interval of $\sim 450\text{--}500$ has not been seen as a single quantum and cannot be identified. If part of the assignment is made as 1_0^2 then the remainder is $\sim 446\text{ cm}^{-1}$, i.e., $2 \times \nu_7'$ but this is unlikely because ν_7 is not seen in two quanta—when it transforms like a_1 . The vibration ν_2 is to be expected, or possibly an increase in ν_3 , and one of these may account for the extra interval. It is also worth observing that $\nu_{00} + 446$ would be found on the high frequency edge of 4_0^3 but such a band, particularly if weak because of the Franck-Condon factors, might easily go unnoticed until three or four quanta of ν_4' later, when it might easily become merged or be swamped by the 1_0^1 band at $18\,270\text{ cm}^{-1}$. The fourth origin is more tentative and, once again, it starts under a phonon band—the band at 5403 \AA . This band suddenly increases in intensity over and above the usual ratio of the phonon:parent and the fact that this occurs at a frequency interval of $\sim \nu_1' + \nu_7'$ from the system origin, makes it very likely that such an origin does, in fact, exist. ($\Delta\nu = 1255\text{ cm}^{-1}$ and $\nu_1' + \nu_7' = 1022 + 223 \equiv 1245\text{ cm}^{-1}$. It is difficult to measure accurately the position of the bands of this progression because of their overlap with the phonon modes associated with the progression $4_0^n 7_0^1 - (n = 7 \rightarrow 10)$, and it is for this reason that the assignment cannot be made unambiguous.)

The spectrum of the crystal thus consists of long progressions of ν_4' usually with the intensity maximum in the fifth or sixth quantum based upon well-spaced origins, and it is this which leads to the regularity observed in the spectrum

together with the complexity caused by the large amount of overlapping of the long progression based upon one origin, with those based upon another. The appearance of two quanta of a crystal mode accompanying every molecular band also leads to some overlapping and consequent complexity. In addition, it must be remembered that the spectrum is really a spectrum of three separate molecules, viz., $\text{CrO}_2\text{Cl}^{35}\text{Cl}^{35}$, $\text{CrO}_2\text{Cl}^{35}\text{Cl}^{37}$ and $\text{CrO}_2\text{Cl}^{37}\text{Cl}^{37}$ with the relative intensities 9:6:1 respectively. This has the effect of broadening the bands as higher and higher quanta are observed.

It is of some interest to comment upon the temperature dependence of the color of liquid and solid chromyl chloride. At room temperature the liquid is a very deep red, as also is a long path length of the vapor, and this color changes to a very much lighter orange red at -80°C and to a slightly more orange color at 77°K , there being no further change down to 4°K . The color change is simply a reflection of the fact that absorption system II has an extensive array of vibrationally "hot" bands to longer wavelengths of the origin at 5796 \AA . At room temperature, these bands absorb appreciably in the liquid down to $\sim 6400 \text{ \AA}$, thus giving the liquid its deep red color. When the liquid is cooled to -80°C (it does not freeze until -96.5°C), the 140-cm^{-1} vibration, which is the one mainly responsible for the intensity, is depopulated markedly in its higher quantum levels and the "edge" of the absorption shifts back to about 5800 \AA , i.e., back nearly to the origin—and the color changes distinctly during this process.

One great difference between the spectrum of both the vapor and/or the solution spectrum and the spectrum of the crystal concerns system III. As Fig. 1 shows, and the vapor spectrum also shows (ϵ), system III probably has a maximum at $\sim 4130 \text{ \AA}$ and has $\epsilon_{\text{max}} \sim 900$. The crystal spectrum, on the other hand (see Fig. 4), does not absorb strongly (i.e., with $\epsilon_{\text{max}} \geq 70$) until $\sim 3800 \text{ \AA}$ and is completely different from the solution or vapor in this respect. Such characteristics suggest a rather strong molecule—molecule interaction of the Davydov type and it would be interesting to compare the actual spectrum with one calculated for the molecular crystal once the crystal structure of chromyl chloride becomes available.

Finally, no evidence has been found to support the "repulsive upper state" hypothesis advanced by Shkapenko (8) and discussed by Helmholtz *et al.* (12). It is quite clear from the frequencies of the bands found that Schkapenko's postulate was formulated to account for an anharmonicity which does not exist. The bands do become somewhat broader at shorter wavelengths because of a number of factors already discussed above, but the rate of convergence is very slow indeed. This fact is also completely supported by the results of the analysis of CrO_2Cl_2 vapor (ϵ).

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REFERENCES

1. A. C. S. VAN HEEL, *Verslag Akad. Wet. Amsterdam* **35**, 1112 (1926); *Proc. Amst. Acad.* **30**, 95 (1927).
2. R. VON RITSCHL, *Z. Physik* **42**, 172 (1927).
3. R. DE L. KRONIG, A. SCHAAFSMA, AND P. K. PEERLKAMP, *Z. Physik. Chem.* **822**, 323 (1933).
4. P. K. PEERLKAMP, *Physica* **1**, 150 (1933).
5. D. S. ALDERDICE, Ph.D. thesis, University College (London), 1963.
6. D. S. ALDERDICE, T. M. DUNN, AND K. P. LANINI (to be published).
7. W. A. HARTFORD AND M. DARRIN, *Chem. Rev.*
8. G. SHKAPENKO, *J. Chim. Phys.* **47**, 22 (1950).
9. W. E. HOBBS, *J. Chem. Phys.* **28**, 1220 (1958).
10. H. STAMMREICH, K. KAWAI, AND Y. TAVARES, *Spectrochim. Acta* p. 438 (1959).
11. F. A. MILLER, G. L. CARLSON, AND W. B. WHITE, *Spectrochim. Acta* p. 709 (1959).
12. L. HELMHOLZ, H. BRENNAN, AND M. WOLFSBERG, *J. Chem. Phys.* **23**, 853 (1955).