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# Linearly Polarised Spectra, Stark Effect and Uniaxial Stress in the Potassium Dichromate Crystal

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The single crystal absorption spectrum of $K_2Cr_2O_7$ has been recorded in the region 18 000 – 19 000 $cm^{-1}$ and the effects of an electric field and an uniaxial stress have been investigated. The spectrum is interpreted in terms of eight chromophores of the type $O_3CrO^-$ related two and two by inversion. No resonance interaction in the unit cell was observed, neither between the two chromophores of one $Cr_2O_7^{2-}$ ion nor between two chromophores related by inversion symmetry.

Potassium dichromate, $K_2Cr_2O_7$, grows in large orange crystals belonging to the triclinic crystal system.[1] The unit cell contains four molecules related two and two by inversion. There is no other symmetry in the unit cell and it thus contains two asymmetric units and four basically different chromium atoms.

Teltow [2] has given a very detailed experimental description of the single crystal spectrum of $K_2Cr_2O_7$ in the region 18 100 – 19 200 $cm^{-1}$. A large number of very sharp lines were reported but no assignment was given.

More recently Butowiez [3] reported new measurements of the spectrum in the same region. It should be noted that although Butowiez claims that his spectra have been recorded in the same manner as those of Teltow, it is clear that the spectra denoted as $\vec{E}\parallel\vec{\alpha}$, $\vec{E}\parallel\vec{\beta}$, and $\vec{E}\parallel\vec{\gamma}$ by Butowiez corresponds to $\vec{E}\parallel\vec{\beta}$, $\vec{E}\parallel\vec{\alpha}$, and $\vec{E}\parallel\vec{\gamma}$, respectively, in Ref. 2 ($\vec{\alpha}$, $\vec{\beta}$ and $\vec{\gamma}$ are the crystal optical directions). On the basis of the application of a hydrostatic pressure to the crystal Butowiez assigned several of the lines as pure electronic transitions and the rest as vibrational structure. The exact nature of these electronic transitions were not specified by Butowiez except for saying that they corresponded to transitions to the $^1T_1$ state of the tetrahedral $CrO_4^{2-}$ ion split by the low crystal symmetry.

After the recent success in the application of the pseudo-Stark effect in assignments and the study of resonance interactions in potassium chlorochromate,[4,5] it was thought that a better understanding of the electronic spectrum of $K_2Cr_2O_7$ could be obtained by this method.

## EXPERIMENTAL

Large perfect single crystals of $K_2Cr_2O_7$ could easily be grown by slowly lowering the temperature of a saturated solution. The crystals were examined by X-ray crystallography. Crystals exhibiting different faces were used: one shows the natural {100} faces, and others were cut and polished with the crystallographic *b*- and *c*-axis, respectively, perpendicular to the face. Since the angle between the *b*- and *c*-axis is $\alpha \simeq 90°$ the three faces are orthogonal. Crystal thicknesses varied from 0.1 to 1.0 mm.

The spectroscopic measurements were made on a Jena Zeiss 2 m grating spectrograph, using the double pass mode (dispersion $\simeq$ 3.69 Å/mm). Spectra were recorded on Kodak Tri-X and Ilford HP-4 panchromatic film at pumped liquid helium temperatures with the crystals completely immersed in liquid helium. The Stark apparatus was described in Ref. 4 and the stress apparatus in Ref. 6. Both are essentially unchanged.

A D.C. Stark field of $2 \times 10^7$ V $m^{-1}$ could be obtained when special care was taken while mounting the crystals. It is important to avoid scratches and dust on the $SnO_2$-surface since this might cause electrical breakdown.

*Table 1.* $K_2Cr_2O_7$: Line polarisations, Stark splittings ($cm^{-1}$ at $|V_0| = 10^7$ $Vm^{-1}$) and stress shifts ($cm^{-1}$ at $4.9 \times 10^7$ N $m^{-2}$). +, observed; −, not observed; w, weak; vw, very weak.

| Line frequency ($cm^{-1}$) | Line polarisations | | | | | | Stark splittings | | | Stress shifts |
|---|---|---|---|---|---|---|---|---|---|---|
| | light ⊥ (100) | | light ∥ [010] | | light ∥ [001] | | Field direction | | | |
| | $\vec{E}\parallel\vec{\alpha}'$ | $\vec{E}\parallel\vec{\gamma}'$ | $\vec{E}\parallel\vec{\alpha}'$ | $\vec{E}\parallel\vec{\gamma}'$ | $\vec{E}\parallel\vec{\alpha}'$ | $\vec{E}\parallel\vec{\gamma}'$ | $\vec{V}_0\perp(100)$ | $\vec{V}_0\parallel[010]$ | $\vec{V}_0\parallel[001]$ | |
| 18 170.8 | + | − | − | w | + | − | 2.59 | 4.92 | 3.65 | 1.4 |
| 18 361.9 | vw | − | − | w | + | − | − | − | 3.34 | − |
| 18 437.7 | + | w | − | w | + | − | 2.52 | 5.12 | 3.41 | 1.4 |
| 18 503.4 | − | + | w | + | + | w | 2.74 | 4.00 | 2.61 | 1.5 |
| 18 589.6 | + | w | + | − | + | − | 3.55 | 3.05 | 2.30 | 9.3 |
| 18 689.6 | + | w | + | − | | w | 4.75 | 1.52 | 4.38 | −4.2 |
| 18 712.0 | + | − | − | + | | − | 2.34 | 4.64 | − | − |
| 18 713.0 | − | + | + | − | | + | 4.34 | 0 | 3.89 | − |
| 18 731.6 | + | + | + | + | | + | 2.30 | 2.32 | 2.70 | − |
| 18 742.0 | + | + | + | + | | + | 1.81 | 1.02 | 5.53 | − |
| 18 915.7 | | | | | | + | − | − | 5.20 | − |

## SPECTRA

Spectra were taken with the light polarised along the extinction directions on each of the three types of crystals. These directions are not the crystal optical directions $\vec{\alpha}$, $\vec{\beta}$, and $\vec{\gamma}$, and the line intensities therefore do not correspond to those of Teltow and Butowiez. Otherwise, the obtained spectra agree completely with those of Refs. 2 and 3. The dispersion of the extinction directions can be neglected over the small wavelength region investigated.

Only the sharp lines of the spectrum have been studied. The results of the polarised spectra are given in Table 1. Here $\vec{\alpha}'$ and $\vec{\gamma}'$ are the extinction directions with the smallest and the largest, respectively, index of refraction on the particular face of the crystal. Notice that $\vec{\alpha}'$ does *not* represent the same direction on two different faces. Polarisation data of two different columns in Table 1 should therefore not be compared directly.

The Stark effect of the crystal was measured with the electric field along three mutually orthogonal directions. All lines were observed to split into two and only two components. As for $KCrO_3Cl$ [4,5] the splitting is symmetric and linear, and the components have equal intensity. The observed splittings are given in Table 1 and are believed to be accurate to within $\pm 0.15$ $cm^{-1}$.

Spectra were taken with the light propagating perpendicularly to the (100) face when an uniaxial stress was applied along the crystallographic *b*-axis. A stress of $5.9 \times 10^7$ N $m^{-2}$ could be obtained before the crystal shattered. None of the lines show a splitting as a result of the stress. Only a linear shift was observed. Table 1 gives the shifts at $4.9 \times 10^7$ N $m^{-2}$ obtained from a linear fitting of the experimental points from three different crystals, all giving identical results. The accuracy is $\pm 0.8$ $cm^{-1}$. Rather thick crystals ($\sim 0.8$ mm) were used in these experiments. The shifts of the high energy lines could therefore not be observed because the lines become obscured by the continuous absorption of the band.

## DISCUSSION

Miskowski *et al.*[7] suggest that it is useful to consider the $Cr_2O_7^{2-}$ ion as two separate chromophores of the type $O_3CrO^-$, and they state that the spectra of $K_2Cr_2O_7$ and $KCrO_3Cl$ are very similar, after due allowance has been made in the $Cr_2O_7^{2-}$ spectrum for the additional complication of the triclinic unit cell with four independent chromium centres. With the present measurements we can see more accurately the content of these ideas.

On closer inspection of Table 1 it is noticed that the lines at 18 170.8, 18 361.9, 18 437.7, and 18 712.0 $cm^{-1}$ show identical Stark effect and polarisation. It is therefore reasonable to assume that the first line is a pure electronic transition and the three other lines are vibrations added onto this origin. The vibrational

intervals are 191, 267, and 541 $cm^{-1}$. In $KCrO_3Cl$ vibrational intervals at 195, 245, and 568 $cm^{-1}$ were found.

In $KCrO_3Cl$ the site group splitting of the lowest $^1E$ ($C_{3v}$) state was 330 $cm^{-1}$. In $K_2Cr_2O_7$ a line 332 $cm^{-1}$ above the first electronic transition, *i.e.* at 18 503.4 $cm^{-1}$ is found. Its polarisation and Stark effect is different from that of the 0 – 0 transition at 18 170.8 $cm^{-1}$. The two lines at 18 170.8 and 18 503.4 $cm^{-1}$ could therefore be assigned to the two components of a split $^1E$ ($C_{3v}$) state.

Thus we see how similar a part of the $K_2Cr_2O_7$ spectrum is to the $KCrO_3Cl$ spectrum. This indicates that the spectrum must be attributed to a chromophore very similar to the $CrO_3Cl^-$ chromophore, *i.e.* the $O_3CrO^-$ chromophore, with the important implication that the interaction between the two $O_3CrO^-$ chromophores of a $Cr_2O_7^{2-}$ ion is small. If the spectrum were to be interpreted in terms of a $Cr_2O_7^{2-}$ chromophore one would expect to observe the vibrations from the whole $Cr_2O_7^{2-}$ ion and not just those originating from one moiety.

If the idea about the separate $O_3CrO^-$ chromophores is accepted, then the next line in the spectrum at 18 589.6 $cm^{-1}$ together with the line at 18 915.7 $cm^{-1}$ could be the components of the first $^1E$ ($C_{3v}$) state of one of the other chromophores. The splitting is 326 $cm^{-1}$ which agrees well with the other values.

The lines at higher energy should be assigned to still other chromophores in the unit cell. It is, however, clear that the higher energy part of the spectrum is very complicated and it is therefore very difficult to make reasonable assignments.

Qualitatively the observed Stark effect can be explained satisfactorily. The eight individual $O_3CrO^-$ chromophores in the unit cell are related two and two by the inversion symmetry. Without the electric field the spectra originating from each member in a pair coincide. The electric field destroys the symmetry of the crystal and the lines will split. Since inversion is the only symmetry in the crystal, the lines will split into two and only two components exactly as observed. The degeneracy of the chromophores related by inversion symmetry shows that there is no resonance interaction across the inversion centre.

The model of individual $O_3CrO^-$ chromophores is confirmed by the stress experiments. Because the site symmetry of each chromophore is $C_1$, all electronic states will be non-degenerate. The only degeneracy that occurs in the unit cell is the degeneracy with respect to inversion. However, a uniaxial stress does not break down inversion symmetry and will therefore not lift this degeneracy. Instead, the stress will cause a slight change in the crystal field. As a result the lines will shift, but no splitting is expected. This is exactly what is observed. Furthermore, the stress experiment shows that the lines at 18 170.8, 18 589.6, and 18 689.6 $cm^{-1}$ correspond to different electronically excited states because the shifts are different. Also the stress experiment confirms that the line at 18 437.7 $cm^{-1}$ is a vibration built onto the first electronic origin at 18 170.8 $cm^{-1}$, because these two lines show the same shift.

It is worth noticing the strength of the combined action of polarised spectra and Stark effect as a tool for assignments. Butowiez assigned the line at 18 712.0 $cm^{-1}$ to a separate electronic transition, but our measurements show that this line is a vibration on the first electronic origin at 18 170.8 $cm^{-1}$. This assignment is in fact confirmed by Butowiez' own measurements of the effect of a hydrostatic pressure which shows that both lines experience the same shift. Furthermore, our measurements show clearly that the two lines at 18 712.0 and 18 713.0 $cm^{-1}$ are indeed separate lines, a fact which both Teltow [2] and Butowiez have been unable to discover because they have only observed the polarised spectra.

In conclusion, the similarity of the $KCrO_3Cl$ and $K_2Cr_2O_7$ spectra should be stressed. In both cases the resonance interaction is very small and the factor group splitting is less than the line width ($\sim 1.5$ $cm^{-1}$). All data can be explained in terms of orientationally degenerate one-site exciton states.

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