Theoret. chim. Acta (Berl.) 12, 325—329 (1968)

Relationes

Low Temperature Absorption Spectra of $CrO_4^=$ in K_2SO_4 and $VO_4^≡$ in $Na_3PO_4 \cdot 12H_2O$

J. C. DUINKER* and C. J. BALLHAUSEN

Kemisk Laboratorium IV, H. C. Ørsted Institutet, The University of Copenhagen, Denmark

Received September 30, 1968

The polarized absorption spectrum of the chromate ion has been measured at liquid hydrogen and helium temperatures. With chromate dissolved in K_2SO_4 evidence is found for two orbitally allowed $^1A_1 \rightarrow {}^1T_2$ electronic absorption bands. The first band is split into three sublevels with the 0–0 lines located at 26,316 cm^{-1}, 26,441 cm^{-1} and 26,610 cm^{-1}. Built upon the 0–0 lines is seen a simple progression in quanta of 783 cm^{-1}. The second transition is nearly featureless, and is found at 34,000 cm^{-1} to 44,000 cm^{-1}. The two bands are assigned as primarily $t_1 \rightarrow 2e$ and as $3t_2 \rightarrow 2e$ respectively.

$VO_4^≡$ dissolved in $Na_3PO_4 \cdot 12H_2O$ showed at liquid nitrogen temperature a broad featureless band found between 30,000 and 40,000 cm^{-1}.

Das polarisierte Absorptionsspektrum des Chromations wurde bei den Temperaturen des flüssigen Wasserstoffs und Heliums gemessen. Für Chromat in K_2SO_4 werden zwei erlaubte Absorptionsbanden $^1A_1 \rightarrow {}^1T_2$ gefunden. Die erste Bande ist dreifach aufgespalten, ihre 0–0 Linien liegen bei 26316 cm^{-1}, 26441 cm^{-1} und 26610 cm^{-1}. Von den 0–0 Linien ausgehend zeigt sich eine einfache Zunahme der Werte um 783 cm^{-1}. Der zweite Übergang ist nahezu strukturlos, er liegt zwischen 34000 cm^{-1} und 44000 cm^{-1}. Die beiden Banden werden überwiegend $t_1 \rightarrow 2e$ bzw. $3t_2 \rightarrow 2e$ zugeordnet.

$VO_4^≡$ in $Na_3PO_4 \cdot 12H_2O$ zeigt bei der Temperatur des flüssigen Stickstoffs eine breite strukturlose Bande zwischen 30000 und 40000 cm^{-1}.

Le spectre d'absorption en lumière polarisée de l'ion chromate a été mesuré aux températures de l'hydrogène et de l'hélium liquide. Pour le chromate dissous dans K_2SO_4 on met en évidence deux bandes d'absorption électronique de transition orbitale permise $^1A_1 \rightarrow {}^1T_2$. La première bande est séparée en trois sous niveaux dont les raies 0–0 se trouvent à 26,316 cm^{-1}, 26,441 cm^{-1} et 26,610 cm^{-1}. A partir des raies 0–0 on distingue une période de 783 cm^{-1}. La seconde bande est presque non structurée et s'étend de 34,000 cm^{-1} à 44,000 cm^{-1}. Les deux bandes sont décrites comme $t_1 \rightarrow 2e$ et $3t_2 \rightarrow 2e$ respectivement.

$VO_4^≡$ dissous dans $Na_3PO_4 \cdot 12H_2O$ révèle à la température de l'azote liquide une large bande sans structure entre 30,000 et 40,000 cm^{-1}.

Introduction

The extensive theoretical calculations [1, 2, 3] of the electronic structures of the metal oxycations which take place in this laboratory makes it highly desirable to have good experimental electronic spectra of these ions. So far we have published the absorption spectrum [4] of MnO_4^-, and in the present note we shall reinvestigate $CrO_4^=$ and $VO_4^≡$. As for MnO_4^- larger and smaller deviations from the old work of Teltow [5] have been observed. However, we shall not here perform a closer analysis of these differences, which undoubtedly are due to Teltow's less advanced instrumentation. The used experimental techniques were

---

* On leave of absence from Anorganisch Chemisch Laboratorium der Universiteit, Amsterdam.

completely analogous to those used for MnO_4^-, and reference is made to this paper [4] for details.

Results

The electronic spectrum of K_2CrO_4 dissolved in K_2SO_4 appears to show two major bands, Fig. 1. The first stretches from 26,000 cm^{-1} to 32,000 cm^{-1} and has a well developed vibrational structure. The second band system stretches from 34,000 cm^{-1} to 44,000 cm^{-1} and shows only a vague fine structure. In order to see whether "forbidden" bands were located on the red side of the first system several crystals of different concentrations were scanned at room- and liquid nitrogen temperatures down to 14,500 Å (7,000 cm^{-1}). With very concentrated crystals the chromate showed a very weak band at 7,200 cm^{-1}. This band appears to be a vibrational overtone. No signs were seen of either orbitally or spin "forbidden" bands.

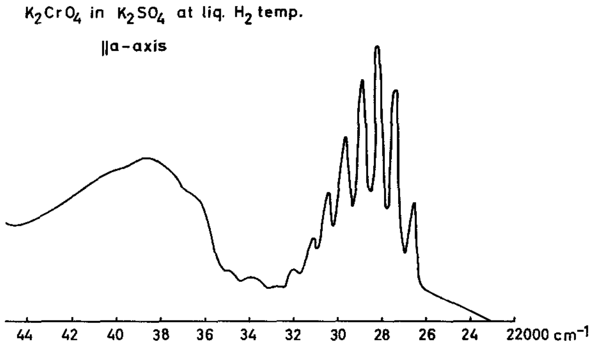

Fig. 1. Overall view of the $CrO_4^=$ spectrum at liquid hydrogen temperature

The site symmetry of the sulphur in the K_2SO_4 lattice is only [6] C_s. We shall assume that chromium occupies the same place as sulphur in a mixed crystal. The orbitally allowed transition ${}^1A_1 \rightarrow {}^1T_2$ in T_d symmetry is therefore expected to split into three bands, reflecting the low site group symmetry. The absorption spectrum of the first chromate band system (Fig. 2) has been recorded with the electric vector parallel to the b and c directions of the host K_2SO_4 lattice. Incidentally the a, b and c values of the mixed crystal agreed exactly with the values for the pure crystals [6].

Disregarding the weak "red" shoulder at 26,344 cm^{-1} on the first main peak of the c axis spectrum as due to incomplete polarizations we notice that the two major peaks are found at 26,441 cm^{-1} and 26,610 cm^{-1} with a separation of 169 cm^{-1}. This pattern is repeated at 27,223 cm^{-1} and 27,385 cm^{-1} and again at higher wavenumbers. The two peaks are seen to have equal intensities.

The vibrations associated with the $CrO_4^=$ unity in the ground state are [7] $\nu_1(A_1) = 847\ cm^{-1}$, $\nu_2(E) = 348\ cm^{-1}$, $\nu_3(T_2) = 884\ cm^{-1}$ and $\nu_4(T_2) = 368\ cm^{-1}$. The separation between the major peak systems of $\sim 780\ cm^{-1}$ is therefore interpreted (Table) as a progression in the totally symmetric breathing frequency of the $CrO_4^=$ unit. That the breathing frequency is somewhat smaller in the excited state than in the ground state follows from the fact that for this state we have transferred a non-bonding electron to an antibonding orbital. With the two peaks in each system having equal intensity, and having a separation of $\sim 160\ cm^{-1}$, it seems reasonable to interpretate the lines at $26{,}441\ cm^{-1}$ and $26{,}610\ cm^{-1}$ as the 0–0 lines of two components of ${}^1A_1 \rightarrow {}^1T_2$ separated by $169\ cm^{-1}$.

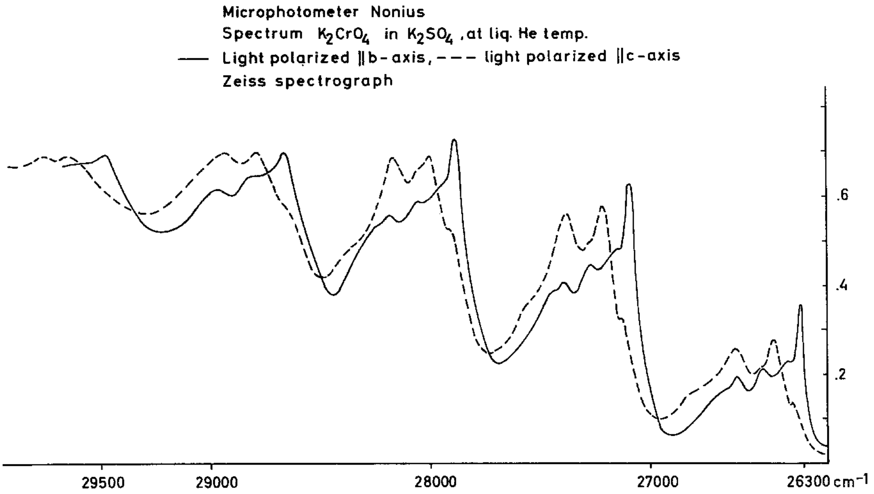

Fig. 2. The first band of $CrO_4^=$ in two different polarizations at liquid helium temperature

Table. *Measured and calculated absorption peaks in first band of* $CrO_4^=$

$\parallel b$ cm^{-1}	calculated[a]	assignment	$\parallel c$ cm^{-1}	calculated[b]	assignment	$\parallel c$ cm^{-1}	calculated[c]	assignment
26,316	23,316	A'	26,441	26,441	A''	26,610	26,610	A'''
27,100	27,105	$A'+\nu_1$	27,223	27,224	$A''+\nu_1$	27,385	27,386	$A'''+\nu_1$
27,894	27,894	$A'+2\nu_1$	28,010	28,007	$A''+2\nu_1$	28,167	28,162	$A'''+2\nu_1$
28,670	28,683	$A'+3\nu_1$	28,791	28,790	$A''+3\nu_1$	28,939	28,938	$A'''+3\nu_1$
29,472	29,472	$A'+4\nu_1$						

[a] $\nu_1 = 789\ cm^{-1}$
[b] $\nu_1 = 783\ cm^{-1}$
[c] $\nu_1 = 776\ cm^{-1}$
Average value of $\nu_1 = 783\ cm^{-1}$

With the electric vector polarized parallel to *b*, we see one major peak followed by some vibrational structure. This pattern is repeated throughout the band system. The separation between the major peaks is again $\sim 789\ cm^{-1}$, corresponding to the totally symmetric frequency. We interpretate the sharp peak at $26{,}316\ cm^{-1}$ as the 0–0 line of the third component of the split ${}^1A_1 \rightarrow {}^1T_2$ transition. The total splitting of the 0–0 lines for the first ${}^1A_1 \rightarrow {}^1T_2$ transition is thus $294\ cm^{-1}$.

The $\parallel b$ polarized peak at 26,603 cm^{-1} and the corresponding peaks at higher wavenumbers is within the experimental uncertainties seen to correspond with the $\parallel c$ polarized peak at 26,610 cm^{-1}. This peak thus shows up in both polarizations. On the other hand we see also particularly in the $\parallel b$ spectrum superimposed upon the $0-n$ lines some vibrations in quanta of 50 cm^{-1} and ~ 170 cm^{-1}. That these are to be assigned as lattice vibrations and not as vibrations associated with the $CrO_4^=$ units is suggested by comparing their values with the vibrational frequencies of $CrO_4^=$.

With regard to the second chromate system we find that the vibrational structure is so slightly pronounced that a closer analysis is impossible.

The $VO_4^{\equiv}$ ion dissolved in $Na_3PO_4 \cdot 12H_2O$ showed only a very broad, completely featureless, band stretching from 30,000 cm^{-1} to 40,000 cm^{-1} (Fig. 3). Due to experimental difficulties (the crystals dehydrated) this system could only be investigated down to liquid nitrogen temperature.

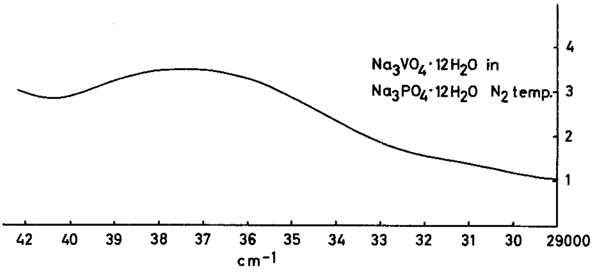

Fig. 3. Absorption spectrum of $VO_4^{\equiv}$

Discussion

The first chromate band system seems completely to resemble the first band system in the isoelectronic MnO_4^- ion [4]. We therefore likewise interpretate [1, 2] this system as a $t_1 \to 2e\,(^1A_1 \to {}^1T_2)$ band, split in the 0–0 lines by 294 cm^{-1} due to "natural" distortions and/or site group splittings. The second chromate band system has a magnetic dichroism [8] which is very close to that of band 3 of MnO_4^-, confirming their common nature. The permanganate band system is interpreted by Dahl and Johansen [2] as mostly $3t_2 \to 2e$ $(^1A_1 \to {}^1T_2)$, and we shall assume the same assignment to hold true for chromate.

An explicit chromate calculation has, however, been performed by Dahl and Johansen [3] which indicates that the transitions $3t_2 \to 2e$ $(^1A_1 \to {}^1T_2)$ should be placed at 34,000 cm^{-1} and $t_1 \to 2e$ $(^1A_1 \to {}^1T_2)$ at 37,400 cm^{-1}. The low lying transition $t_1 \to 4t_2$ $(^1A_1 \to {}^1T_2)$ should be placed at 46,500 cm^{-1}. It is, however, rather likely that the above $CrO_4^=$ calculations are less reliable than the MnO_4^- assignments [2] and we prefer therefore to draw our conclusions as to the chromate band assignments in analogy with the permanganate assignments.

As to an assignment for the broad featureless 37,000 cm^{-1} $VO_4^{\equiv}$ band our experiments are not of any help. Dahl and Johansen [3] calculated that the $3t_2 \to 3a_1$ $(^1A_1 \to {}^1T_2)$ transition should occur at 37,500 cm^{-1}. The good numerical agreement is, however, not in any way to be taken as a proof of the assignment.

References

1. Dahl, J. P., and C. J. Ballhausen: Advances in Quantum Chemistry **4**, 170 (1968).
2. —, and H. Johansen: Theoret. chim. Acta (Berl.) **11**, 8 (1968).
3. — — Theoret. chim. Acta (Berl.) **11**, 26 (1968).
4. Holt, S. L., and C. J. Ballhausen: Theoret. chim. Acta (Berl.) **7**, 313 (1967).
5. Teltow, J.: Z. physik. Chem. B **43**, 198 (1939).
6. Robinson, M. T.: J. physic. Chem. **62**, 925 (1958).
7. Müller, A., and B. Krebs: Molecular Physics **12**, 517 (1967).
8. Schatz, P. N., A. J. McCaffery, W. Suetaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens: J. chem. Physics **45**, 722 (1966).

Professor Dr. C. J. Ballhausen
Chemical Laboratory IV
H. C. Ørstedinstitutet, Universitetsparken 5
København Ø, Danmark