

Low Temperature Absorption Spectra of KMnO_4 in KClO_4

SMITH L. HOLT* and C. J. BALLHAUSEN

Department of Physical Chemistry, H. C. Ørsted Institute, The University of Copenhagen, Denmark

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The permanganate spectrum has been remeasured at liquid hydrogen and helium temperatures using spectrographs with reasonably high dispersion. Evidence is found for four absorption band systems. The first one is assigned as ${}^1A_1 \rightarrow {}^1T_2$ and displays a great deal of vibrational structure starting with the 0—0 line located at $18,072\text{ cm}^{-1}$. The second transition found at $25,000$ to $30,000\text{ cm}^{-1}$ is rather featureless. The third transition with maximum at $33,000\text{ cm}^{-1}$ shows a simple progression in quanta of 750 cm^{-1} . The fourth band is completely featureless with maximum intensity at $43,500\text{ cm}^{-1}$. These findings are compared with a simplified SCF LCAO MO calculation.

Das Permanganat-Spektrum wurde bei Temperaturen von flüssigem Wasserstoff und Helium unter Verwendung eines ausreichend auflösenden Spektrographen neu vermessen, wobei vier Absorptionssysteme gefunden wurden. Dem ersten von ihnen wurde ein ${}^1A_1 \rightarrow {}^1T_2$ -Übergang zugeordnet; es besitzt eine ausgeprägte Vibrationsstruktur (0—0-Bande bei $18,072\text{ cm}^{-1}$), während das folgende zwischen $25,000$ und $30,000\text{ cm}^{-1}$ kaum eine Struktur zeigt. Der dritte Übergang mit Maximum bei $33,000\text{ cm}^{-1}$ zeigt einfache Progressionen entsprechend Quanten von 750 cm^{-1} . Die vierte Bande schließlich ist vollkommen strukturlos und hat ihr Maximum bei $43,500\text{ cm}^{-1}$. Diesen Daten wurden die Ergebnisse einer einfachen SCF-LCAO-MO-Rechnung gegenübergestellt.

Le spectre du permanganate de potassium a été réétudié aux températures de l'hydrogène et de l'hélium liquide en utilisant des spectrographes à dispersion raisonnablement élevée. On trouve la preuve de la présence de quatre systèmes de bandes d'absorption. Le premier, attribué à ${}^1A_1 \rightarrow {}^1T_2$, possède une forte structure vibrationnelle commençant à la bande 0—0 située à $18,072\text{ cm}^{-1}$. La seconde transition située entre $25,000$ et $30,000\text{ cm}^{-1}$ est plutôt sans structure. La troisième transition avec un maximum à $33,000\text{ cm}^{-1}$ présente une progression simple de 750 cm^{-1} . La quatrième bande est complètement sans structure et a son maximum vers $43,500\text{ cm}^{-1}$. Ces observations sont comparées avec un calcul simplifié SCF LCAO MO.

Introduction

Teltow's old measurements [1, 2] of the line spectra of KMnO_4 dissolved in KClO_4 have been analyzed and interpreted in some detail by WOLFSBERG and HELMHOLZ [3] and BALLHAUSEN [4]. Using two different electronic level schemes as the basis for the analysis, both claimed that a reasonable agreement between theory and experiment could be obtained. The experimental results reported by TELTOW were obtained using a spectrograph with rather small dispersion; as a result some of the spectral details look rather unconvincing. Furthermore since

* NATO Postdoctoral Fellow 1965-66. Present address: Chemistry Department, Polytechnic Institute of Brooklyn, Brooklyn, N. Y., U.S.A.

the electronic structure of the permanganate ion has been the subject of considerable controversy (see e.g. the paper by DAHL and BALLHAUSEN [5]) it was thought worthwhile to repeat and extend some of the old measurements.

Experimental

Measurements were made upon single crystals of $\text{KMnO}_4/\text{KClO}_4$ at 20 °K and 4.2 °K using both a Cary 14 spectrophotometer and a Zeiss 2 m grating spectrograph with dispersion $\sim 6 \text{ \AA/mm}$ in the region of interest. The 20 °K spectra were obtained using a Cryo-Tip liquid cryostat in conjunction with the Cary. The 4.2 °K spectra were recorded using either an immersion dewar in connection with the Zeiss instrument or obtained from a conductively cooled sample, using the Cary 14.

Polarization of the incident light was achieved using a single Glan-Thompson prism for measurements with the Zeiss instrument and with both the sample and reference beams polarized by Glan-Thompson prisms in the Cary 14. Absorption spectra were recorded with the electric vector parallel to both the a and b axis of the mixed crystal. The crystal faces were identified using Teltow's analysis. The positions of the sharp progression maxima are correct to 10 cm^{-1} . For the shoulders and broader bands the positions are in certain ideal cases again correct to 10 cm^{-1} , but not better than $\sim 30 \text{ cm}^{-1}$ in other cases.

Results

The absorption spectrum observed at 4 °K with the electric vector $\parallel b$ is shown in Fig. 1. If this spectrum is compared to the corresponding spectrum of Teltow's, several differences are immediately obvious. First, the weak system reported by TELTOW to occur below $17,000 \text{ cm}^{-1}$ is not observed. While this may be due to an insufficient ratio of KMnO_4 to KClO_4 in our crystals it should be noted that the analogous weak system of bands between $24,500 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$ is observed. Second, TELTOW did not report the moderately broad strong absorption in the $24,500 \text{ cm}^{-1}$ to $30,000 \text{ cm}^{-1}$ region upon which the above weak system is superimposed. Finally the strong band which we observe at $\sim 43,500 \text{ cm}^{-1}$ was likewise not observed by TELTOW.

The strong visible system commencing at $\sim 18,000 \text{ cm}^{-1}$ shows definite differences in detail between the two polarizations. The first "component" in each polarization is shown in Fig. 2. There is also a moderate difference in intensity

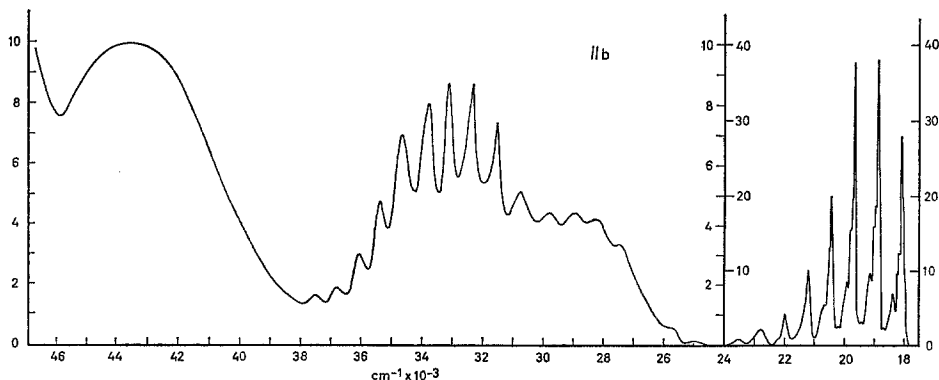


Fig. 1. Absorption spectrum of KMnO_4 dissolved in KClO_4 at liquid helium temperature. The electric vector is parallel to b . Relative extinction coefficient as ordinate

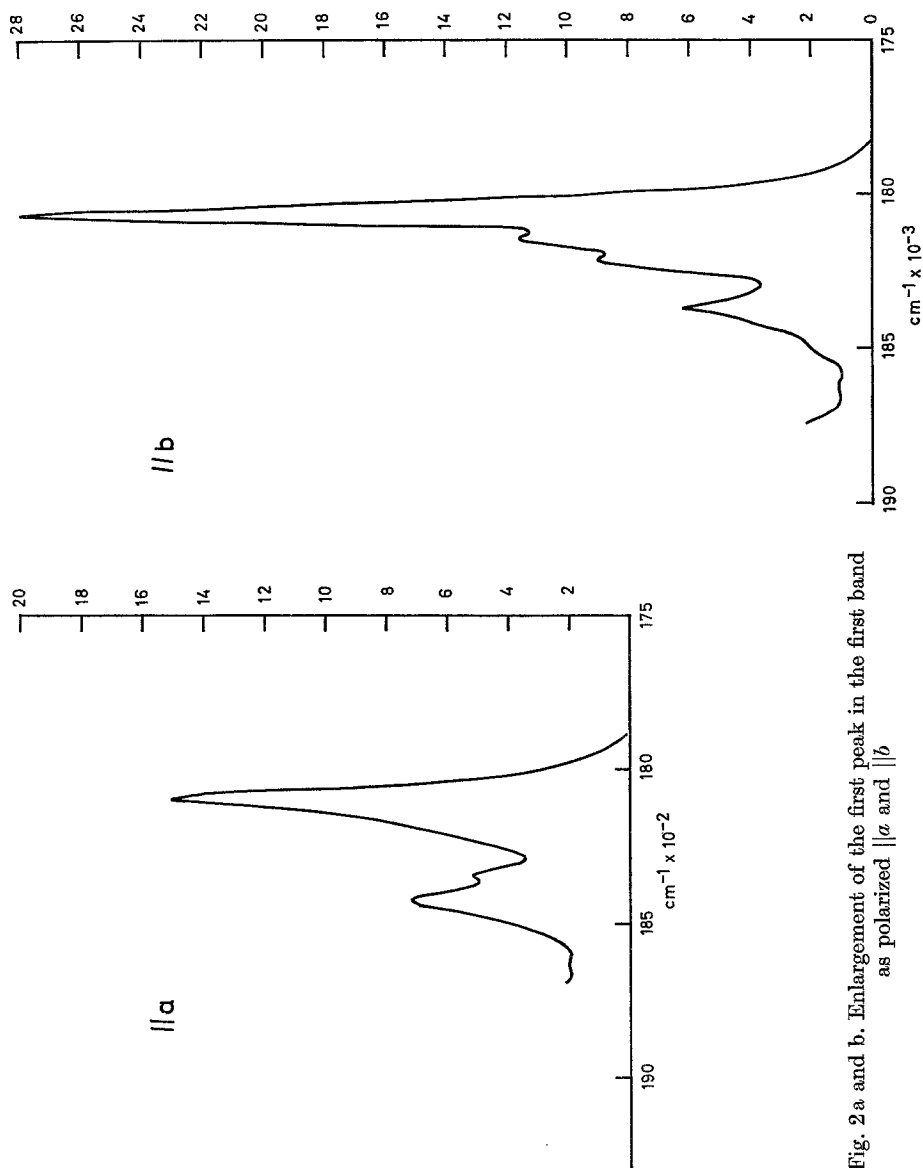


Fig. 2 a and b. Enlargement of the first peak in the first band as polarized $\parallel a$ and $\parallel b$

between the $\parallel a$ and $\parallel b$ polarizations for the first system which is not mirrored by the other strong bands. Between 25,000 and 30,000 cm^{-1} , the low energy absorptions are more prominent in the $\parallel a$ polarization than in the $\parallel b$ while the 28,150, 28,950 and 29,750 cm^{-1} peaks are barely visible $\parallel a$. Above 30,000 cm^{-1} the $\parallel a$ and $\parallel b$ spectra are virtually identical.

The spectrum falls into four regions. The first region goes from 18,000 cm^{-1} to 23,000 cm^{-1} . This part is characterized by a great deal of fine structure. The second region goes from 24,500 cm^{-1} to 30,000 cm^{-1} . Here we find a simple

Table 1. *Measured and calculated absorption peaks in first band (${}^1A_1 \rightarrow {}^1T_2$) system*

a			
Measured Intensity ^a	Frequency	Calculated Frequency ^b	Proposed Assignment
47	18074	18074	$A'(1)$
53	18094	18094	$A'(2)$
15	18345	18346	$A'(1) + \nu_3$
20	18415	18408	$A'(1) + \nu_2$
18	18430	18428	$A'(2) + \nu_2$
5	18623	18618	$A'(1) + 2\nu_3$
		18843	$A'(1) + \nu_1$
85	18849		$A'(1)$ or $A'(2) + \nu_1$ unresolved
		18862	$A'(2) + \nu_1$
27	19114	19114	$A'(1) + \nu_1 + \nu_3$
29	19181	19176	$A'(1) + \nu_1 + \nu_2$
27	19203	19196	$A'(2) + \nu_1 + \nu_2$
8	19388	19386	$A'(1) + \nu_1 + 2\nu_3$
		19610	$A'(1) + 2\nu_1$
77	19611		$A'(1)$ or $A'(2)$ unresolved
		19630	$A'(2) + 2\nu_1$
27	19876	19882	$A'(1) + 2\nu_1 + \nu_3$
24	19957	19964	$A'(2) + 2\nu_1 + \nu_2$
7	20152	20154	$A'(1) + 2\nu_1 + 2\nu_3$
44	20374	20278	$A'(1) + 3\nu_1$
43	20398	20398	$A'(2) + 3\nu_1$
16	20645	20650	$A'(1) + 3\nu_1 + \nu_3$
15	20718	20732	$A'(2) + 3\nu_1 + \nu_2$
5	20916	20922	$A'(1) + 3\nu_1 + 2\nu_3$
		21146	$A'(1) + 4\nu_1$
25	21143		
		21116	$A'(2) + 4\nu_1$
12	21425	21418	$A'(1) + 4\nu_1 + \nu_3$
11	21490	21500	$A'(2) + 4\nu_1 + \nu_2$
		21914	
12	21905		$A'(1) + A'(2) + 5\nu_1$
		21934	
8	22157	22177	$A'(1) + 5\nu_1 + \nu_3$
8	22251	22268	$A'(2) + 5\nu_1 + \nu_2$
7	22667		$A'(1) + A'(2) + 6\nu_1$

^a Calculated with reference to most intense band in polarization ||b.

^b $\nu_1 = 768 \text{ cm}^{-1}$, $\nu_2 = 334 \text{ cm}^{-1}$, $\nu_3 = 272 \text{ cm}^{-1}$.

vibrational progression superimposed upon a featureless (?) broad background. The third region goes from $30,000 \text{ cm}^{-1}$ to $38,000 \text{ cm}^{-1}$ and consists of a single progression in quanta of 750 cm^{-1} . The fourth region goes from $30,000 \text{ cm}^{-1}$ to $46,000 \text{ cm}^{-1}$ and is made up of a broad, featureless absorption band. The integrated intensities of all these bands characterize them as spin allowed transitions. From the general pattern and from the analysis presented below, we feel that we are dealing with four electronic transitions.

Table 1 (Continued) $\parallel b$

Measured Intensity	Frequency	Calculated Frequency ^c	Proposed Assignment
74	18072	18072	A''
35	18138	18139	$A'' + \nu_0$
24	18206	18204	$A'' + 2\nu_0$
14	18353	18350	$A'' + \nu_3$
17	18369		$A'' + 297$
8	18435		$A'' + 297 + \nu_0$
7	18501		$A'' + 297 + 2\nu_0$
5	18633	18628	$A'' + 2\nu_3$
100	18842	18841	$A'' + \nu_1$
59	18905	18907	$A'' + \nu_1 + \nu_0$
43	18972	18973	$A'' + \nu_1 + 2\nu_0$
27	19127	19120	$A'' + \nu_1 + \nu_3$
25	19156		$A'' + \nu_1 + 314$
4	19391	19399	$A'' + \nu_1 + 2\nu_3$
96	19602	19610	$A'' + 2\nu_1$
60	19667	19676	$A'' + 2\nu_1 + \nu_0$
42	19734	19742	$A'' + 2\nu_1 + 2\nu_0$
23	19888	19888	$A'' + 2\nu_1 + \nu_3$
20	19929		$A'' + 2\nu_1 + 327$
6	20614	20166	$A'' + 2\nu_1 + 2\nu_3$
59	20380	20379	$A'' + 3\nu_1$
14	20655	20567	$A'' + 3\nu_1 + \nu_3$
11	20712		$A'' + 3\nu_1 + 332$
27	21145	21148	$A'' + 4\nu_1$
8	21418	21426	$A'' + 4\nu_1 + \nu_3$
10	21915	21917	$A'' + 5\nu_1$

^c $\nu_1 = 769 \text{ cm}^{-1}$; $\nu_3 = 278 \text{ cm}^{-1}$; $\nu_0 = 66 \text{ cm}^{-1}$.

First Band System

The first band system starts at $18,072 \text{ cm}^{-1}$ and has its maximum at about $20,000 \text{ cm}^{-1}$. The vibrational pattern is very complicated resulting in a high degree of complexity. The analysis presented in Tabs. 1 and 2 show that we are dealing with a single electronic transition from the orbitally non-degenerate groundstate to a threefold orbitally degenerate state. By the low site symmetry the upper state is split into three components. Using the nomenclature of Ref. [4] we find for the $\parallel a$ spectrum two origins $A'(1)$ and $A'(2)$ at $18,074 \text{ cm}^{-1}$ and $18,094 \text{ cm}^{-1}$ respectively. $\parallel b$ we find only one origin occurring at $18,072 (A'')$.

Taking now the average of all the relevant vibrations which appear throughout the entire visible system we can identify three different vibrations: $\nu_1 = 768 \text{ cm}^{-1}$, $\nu_2 = 334 \text{ cm}^{-1}$ and $\nu_3 = 272 \text{ cm}^{-1}$. If we first consider the $\parallel a$ spectrum we find built upon $A'(1)$ one quanta of ν_2 at $18,415 \text{ cm}^{-1}$ and two quanta of ν_3 at $18,345 \text{ cm}^{-1}$ and $18,623 \text{ cm}^{-1}$. Built upon the $A'(2)$ origin is one quanta of ν_2 at $18,430 \text{ cm}^{-1}$. These assignments follow those given in Ref. [4].

Following this complicated system there are seven further systems separated by ν_1 . $A'(1) + \nu_1$ and $A'(2) + \nu_1$ are unresolved (and remain unresolved until the

4th member of the series) and their combined maximum occurs at 18,849 cm^{-1} . However, $A'(1) + \nu_1 + \nu_3$ occurs at 19,114 cm^{-1} and $A'(1) + \nu_1 + 2\nu_3$ at 19,388; $A'(1) + \nu_1 + \nu_2$ occurs at 19,181 and what we have assigned as $A'(2) + \nu_1 + \nu_2$ is present as a weak shoulder at 19,203 cm^{-1} . This then is the general pattern throughout. It is of further interest that on the high energy side of all $A'(1)$, $A'(2) + \nu_3$ a broad shoulder occurs. This is probably an unresolved lattice vibration ν_0 .

||b - Within the limits of resolution of the instruments used there is only one origin and that occurs as previously stated at 18,072 (A''). Even though this falls only 2 cm^{-1} from $A'(1)$, the separation is probably real. The ν_0 lattice vibrations are very prominent in this polarization and two members of ν_3 i.e., $A'' + \nu_3$ and $A'' + 2\nu_3$ are seen at 18,350 cm^{-1} and 18,628 cm^{-1} . However, an unresolved problem lies with the peak at 18,369 cm^{-1} and the shoulders at 19,156 cm^{-1} , 19,929 cm^{-1} , etc. This seems to be an anharmonic vibration and appears in both the 20 °K and 4.2 °K spectra. It is possible but not very likely that its position is a function of the intensity of $A'' + \nu_3$. For a full identification of this band see Tab. 1. The (0—0) band and the associated vibrations are pictures in Figs. 2a and 2b.

The Second Band System

The absorption in the region 25,000 cm^{-1} to 30,000 cm^{-1} consists of seven peaks superimposed upon a strong background. From the irregular intensity patterns we feel that we are observing on the high frequency side a superposition of vibrations belonging to the third system on a nearly structureless band. The vibrational structure on the low frequency side is on the other hand most likely associated with the second electronic system.

The Third Band System

A very regular progression in 750 cm^{-1} is observed, the maximum occurring at 33,000 cm^{-1} . There is no doubt that we are only dealing with one electronic transition.

The Fourth Band System

This completely featureless band has its maximum at 43,500 cm^{-1} . Again we are evidently only dealing with one electronic transition.

Discussion

As demonstrated we have found evidence for four spinallowed electronic transitions occurring at 2.3 eV (1st system) 3.5 eV (2. system) 4.0 eV (3. system) and 5.5 eV (4. system). Performing a molecular orbital calculation DAHL and BALLHAUSEN [5] arrived at the level scheme given in abbreviated form in Fig. 3. The calculated transition energies are given in Tab. 2. Notice, however, that in this table the first transition at 2.3 eV has been used to "scale" the *exchange* integrals occurring in the evaluation of $W(^1A_1 \rightarrow ^1X, u \rightarrow v)$.

The interesting feature emerged from the calculation [5] that the $3t_2$ level has 64% ligand π orbital character. The t_1 and to slighter extent the $3t_2$ orbitals can therefore to good approximation be characterized as non bonding ligand π orbitals.

The ($t_1 \rightarrow 2e$) or ($3t_2 \rightarrow 2e$) transitions are therefore expected to resemble each other a great deal, both being $\pi \rightarrow \pi^*$.

That the transition found at 2.3 eV is to be assigned to the orbitally allowed transition ${}^1A_1 \rightarrow {}^1T_2$ ($t_1 \rightarrow 2e$) is by now generally agreed upon [5–9]. From the above it follows then that the 4.0 eV band is associated with a ${}^1A_1 \rightarrow {}^1T_2$ ($3t_2 \rightarrow 2e$) transition. These two bands are so similar in appearance that this seems the only natural conclusion, especially if we remember that $\pi \rightarrow \pi^*$ transitions customary show a great deal of structure.

The assignment of the 5.5 eV system is rather doubtful. However, if the calculation reported in Ref. [5] is to be a guide, it seems natural to assign it to an orbitally forbidden transition involving a promotion of an electron from the bonding $2a_1$ orbital to the antibonding $2e$ orbital.

Table 2. Calculated and measured absorption band maxima for MnO_4^-

Transition	Transition energy eV calculated
$t_1 \rightarrow 2e$	(2.3)
$t_1 \rightarrow 4t_2$	9.3
$3t_2 \rightarrow 2e$	3.1
$1e \rightarrow 2e$	3.5
$2a_1 \rightarrow 2e$	6.5

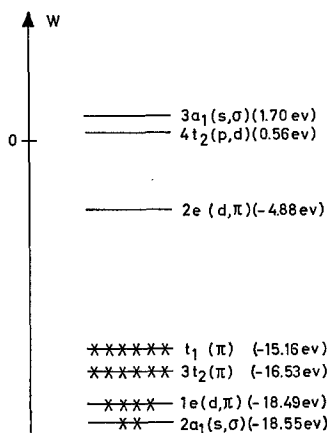


Fig. 3. Part of SCF-LCAO-MO energy diagram for MnO_4^-

The 3.5 eV system is the most difficult one to assign. Again, from a calculational point of view [5], the $1e$ orbital seems to be involved, and very tentatively we interpret it as an orbitally forbidden ($1e \rightarrow 2e$) transition. If we admit the possibility of observing such transitions we must ask why we do not observe ${}^1A_1 \rightarrow {}^1T_1$ ($t_1 \rightarrow 2e$) or the ${}^1A_1 \rightarrow {}^1T_1$ ($3t_2 \rightarrow 2e$) transitions. Actually the last assignment is the one suggested by VISTE and GRAY [6] for the 3.5 eV band. It is, however, likely that configuration interaction between the excited states is important, and that these states are covered or pushed out of the investigated interval. As to the placement on the energy scale we cannot expect any help from the available calculations [5, 6, 7].

The excitation ($t_1 \rightarrow 2e$) produces, as is easily seen, a total number of four states, namely 1T_1 , 1T_2 , 3T_1 and 3T_2 states.

A simple calculation [4] indicates that the order of these levels is $E({}^1T_2) > E({}^1T_1) > E({}^3T_1) \approx E({}^3T_2)$. We would certainly expect a configuration interaction to be able to push 1T_1 even further down. But how far? Has it crossed the spin-triplets? We have scanned the permanganate spectrum all the way down to 8250 cm^{-1} at 20°K and to $12,500 \text{ cm}^{-1}$ at 4.2°K . There seems to be a broad band whose center is about $10,500 \text{ cm}^{-1}$, but it may only be a base line effect. The total integrated intensity of this band is less than 10^{-3} of the main band.

A further investigation of this low-lying band is under way using more advanced techniques and the results will be published in due course.

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Prof. C. J. BALLHAUSEN
Department of Physical Chemistry
H. C. Ørsted Institute
Universitetsparken 5
København Ø, Denmark