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Chemical Laboratory IV, H. C. Ørsted Institute,
The University of Copenhagen, Denmark

A Vibrational Analysis of the MnO_4^- Bands

By

C. J. Ballhausen

Teltow's [*14, 15*] measurements of the permanganate bands are reanalyzed using the level scheme of Ballhausen and Liehr [*2*]. For $KMnO_4$ dissolved in $KClO_4$ the components of the first $^1T_2$ state are found at 18050 cm^{-1}, 18078 cm^{-1} and 18043 cm^{-1}. The breathing frequency of the MnO_4^- unit is in this state 768 cm^{-1}. The electronic origin of the second $^1T_2$ state is found at 30723 cm^{-1} with a breathing frequency of 760 cm^{-1}.

Evidence is further found for a $^1T_1$ state with its split components located at 14446 cm^{-1}, 14526 cm^{-1} and 14600 cm^{-1}. The breathing frequency is here found to be 800 cm^{-1}.

Finally for $KMnO_4$ dissolved in $NaClO_4$ there are indications that one or two spin-triplets are located near 13200 cm^{-1}.

Teltows Messungen des Permanganatspektrums [*14, 15*] werden mit Hilfe des Termschemas von Ballhausen und Liehr [*2*] von neuem analysiert. Für $KMnO_4$ in $KClO_4$ findet man die zum ersten $^1T_2$-Zustand gehörenden Komponenten bei 18050, 18078 und 18043 cm^{-1}. Die Valenzschwingung des MnO_4^- liegt hier bei 768 cm^{-1}. Der Ursprung des zweiten $^1T_2$-Systems wird bei 30723 cm^{-1} gefunden, die dazugehörige Valenzfrequenz ist 760 cm^{-1}.

Bei 14446, 14526 und 14600 cm^{-1} liegen offenbar die Komponenten eines $^1T_1$-Terms, wozu eine Valenzfrequenz von 800 cm^{-1} gehört.

Schließlich findet man für $KMnO_4$ in $NaClO_4$ Anzeichen für ein oder zwei Spin-Tripletts um 13200 cm^{-1}.

Les bandes d'absorption du permanganate, mesurées par Teltow [*14, 15*], sont réanalysées à l'aide d'un système de termes proposé par Ballhausen et Liehr [*2*]. Pour $KMnO_4$ dans $KClO_4$, on trouve les composants du premier état $^1T_2$ à 18050, 18078 et 18043 cm^{-1}. La vibration symétrique du MnO_4^- dans cet état se situe à 768 cm^{-1}. L'origine électronique du second état $^1T_2$ est trouvé à 30723 cm^{-1}, la fréquence oscillatrice correspondante est de 760 cm^{-1}.

Un état $^1T_1$ avec ses composants à 14446, 14526 et 14600 cm^{-1} est mis en évidence, avec une vibration symétrique de 800 cm^{-1}.

Finalement, au cas du $KMnO_4$ dissous dans le $NaClO_4$, il y a des indications pour un ou deux triplets de spin vers 13200 cm^{-1}.

Introduction

In 1938—39 Teltow [*14, 15*] published extensive investigations of the "visible" absorption spectra of the MnO_4^- ion imbedded in various lattices. No interpretation was given of these detailed line spectra before Wolfsberg and Helmholz [*16*] in 1952 presented an analysis of Teltow's data. They concluded that the experimental features of the excited states of the ion agreed with their theoretical calculations.

Nevertheless, in 1958 Ballhausen and Liehr [*2*] suggested on basis of general ideas as to the nature of the bonding that the level scheme of Wolfsberg and Helmholz was in error. Whereas in Wolfsberg and Helmholz's scheme the first empty orbital should be of t_2 symmetry, BALLHAUSEN and LIEHR assumed it to be of e symmetry. In both cases the "first band", located at some 18500 cm^{-1}, should be due to an orbital allowed ${}^1A_1 \rightarrow {}^1T_2$ transition. However, there are great differences between the two proposed level schemes as to the occurence of other low lying states.

WOLFSBERG and HELMHOLZ calculated that states of symmetry ${}^1A_2$, ${}^1E$ and ${}^1T_1$ should be found on the red side of the 18500 cm^{-1} band, and their analysis of TELTOW's data apparently revealed evidence for an ${}^1E$ and a ${}^1T_1$ state. On the other hand, the level scheme of BALLHAUSEN and LIEHR would only yield one singlet state in this range, of T_1 symmetry. Dipole transitions to all of these states are orbitally forbidden in T_d symmetry.

The experimental evidence was therefore in favor of the WOLFSBERG and HELMHOLZ scheme until CARRINGTON et al. [*5*] and SCHONLAND [*12*] showed by paramagnetic resonance methods, that in the manganate MnO_4^{2-} and hypomanganate MnO_4^{3-} ions the additional, unpaired electrons went into a doubly degenerate e orbital. These experiments therefore showed that the first unoccupied orbital in MnO_4^- is an e orbital in agreement with the proposal of BALLHAUSEN and LIEHR. The analysis by CARRINGTON and SCHONLAND [*4*] of the band intensities also substantiated the second level scheme.

This new evidence makes it important to reanalyse TELTOW's data in the region of the orbital forbidden transitions, and this is therefore the aim of the present note. For consistency, we will likewise look at the orbital allowed transitions in order to gain as much information as possible.

First ${}^1A_1 \rightarrow {}^1T_2$ Band

The MnO_4^- ion shows the first broad band at some 18500 cm^{-1}, with an oscillator strength $f \approx 0.03$. This band is assigned as the orbital allowed transition ${}^1A_1 \rightarrow {}^1T_2$, during which a t_1 electron is promoted to the first empty e level. TELTOW found in this region of the spectrum, measuring at the temperature of liquid hydrogen, a long series of band progressions. We shall assume that all of the transitions start out from the lowest vibrational state of the ground state. As the best documentated we first take his measurements of MnO_4^- dissolved in $KClO_4$. The site group symmetry of MnO_4^- is here only C_s, that is we would expect the ${}^1T_2$ level to split up in three states of symmetry A'' and A' (1) + A' (2). With the ground state transforming like A', the transitions $A' \rightarrow A'$ should be observed with the electric vector parallel to the a and c crystal axes. Furthermore the $A' \rightarrow A''$ transition should be seen with the electric vector parallel to the b axis [*16*].

This behaviour is exactly what is found. With the electric vector parallel to a and c, doublets are seen, whereas parallel to b TELTOW only observed singlets. A closer analysis of TELTOW's data (Tab. 1) gives that the electronic origins are located at A' (1): 18050 cm^{-1}, A' (2): 18078 cm^{-1} and A'': 18043 cm^{-1}. The total spread of ${}^1T_2$ due to the lower site symmetry is 35 cm^{-1}. The ${}^1T_2$ level is thus only slightly perturbed.

One would have expected that a Jahn-Teller splitting of the T_2 state should take place. Both e and t_2 vibrational frequencies are capable of causing such a splitting [*1*], but we see no evidence of that it has occurred.

Table 1. *Assignments of the band system* $^1A_1 \to {}^1T_2\,(1)$ *of* MnO_4^- *in* $KClO_4$
Measurements after TELTOW [*14, 15*]

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Measured Intensity	Measured Frequency	Calculated Frequency	Proposed Assignment
55	18051	18051	$A'\,(1)$
60	18076	18076	$A'\,(2)$
11	18332	18331	$A'\,(1) + \nu_3$
22	18400	18401	$A'\,(2) + \nu_2$
1	18613	18611	$A'\,(1) + 2\nu_3$
100	18821	18819	$A'\,(1) + \nu_1$
100	18838	18844	$A'\,(2) + \nu_1$
30	19101	19099	$A'\,(1) + \nu_1 + \nu_3$
35	19163	19169	$A'\,(2) + \nu_1 + \nu_2$
2	19374	19379	$A'\,(1) + \nu_1 + 2\nu_3$
80	19592	19587	$A'\,(1) + 2\nu_1$
24	19865	19867	$A'\,(1) + 2\nu_1 + \nu_3$
22	19938	19937	$A'\,(2) + 2\nu_1 + \nu_2$
2	20141	20147	$A'\,(1) + 2\nu_1 + 2\nu_3$
50	20352	20355	$A'\,(1) + 3\nu_1$
13	20625	20635	$A'\,(1) + 3\nu_1 + \nu_3$
12	20703	20705	$A'\,(2) + 3\nu_1 + \nu_2$
19	21125	21123	$A'\,(1) + 4\nu_1$
6	21403	21403	$A'\,(1) + 4\nu_1 + \nu_3$
5	21476	21473	$A'\,(2) + 4\nu_1 + \nu_2$
7	21881	21891	$A'\,(1) + 5\nu_1$
2	22213	22241	$A'\,(2) + 5\nu_1 + \nu_2$
3	22632	22659	$A'\,(1) + 6\nu_1$
1	23396	23427	$A'\,(1) + 7\nu_1$
0.3	24160	24195	$A'\,(1) + 8\nu_1$

|| b

Measured Intensity	Measured Frequency	Calculated Frequency	Proposed Assignment
65	18043	18043	A''
24	18121	18121	$A'' + \nu_0$
14	18194	18194	$A'' + 2\nu_0$
8	18350	18345	$A'' + \nu_2$
0.5	18602	18600	$A'' + \nu_2 + \nu_3$
100	18813	18811	$A'' + \nu_1$
47	18893	18889	$A'' + \nu_0 + \nu_1$
28	18961	18967	$A'' + 2\nu_0 + \nu_1$
14	19115	19113	$A'' + \nu_1 + \nu_2$
1	19368	19368	$A'' + \nu_1 + \nu_2 + \nu_3$
85	19579	19579	$A'' + 2\nu_1$
36	19675	19657	$A'' + \nu_0 + 2\nu_1$
24	19723	19735	$A'' + 2\nu_0 + 2\nu_1$
12	19871	19881	$A'' + 2\nu_1 + \nu_2$
11	19916	19912	$A'' + \nu_0 + 2\nu_1 + \nu_3$
0.5	20132	20136	$A'' + 2\nu_1 + \nu_2 + \nu_3$
32	20348	20347	$A'' + 3\nu_1$
6	20637	20649	$A'' + 3\nu_1 + \nu_2$
5	20693	20680	$A'' + \nu_0 + 3\nu_1 + \nu_3$
14	21124	21115	$A'' + 4\nu_1$
6	21880	21883	$A'' + 5\nu_1$
3	22645	22651	$A'' + 6\nu_1$
1	23413	23419	$A'' + 7\nu_1$

$\parallel c$

Measured Intensity	Measured Frequency	Calculated Frequency	Proposed Assignment
60	18049	18049	$A'\,(1)$
60	18079	18079	$A'\,(2)$
13	18128	18127	$A'\,(1) + \nu_0$
9	18193	19205	$A'\,(1) + 2\nu_0$
17	18353	18351	$A'\,(1) + \nu_2$
9	18391	18381	$A'\,(2) + \nu_2$
2	18500	18507	$A'\,(1) + 2\nu_0 + \nu_2$
2	18620	18621	$A'\,(1) + \nu_2 + \nu_3$
100	18817	18817	$A'\,(1) + \nu_1$
100	18840	18847	$A'\,(2) + \nu_1$
22	18964	18973	$A'\,(1) + 2\nu_0 + \nu_1$
14	19112	19119	$A'\,(1) + \nu_1 + \nu_2$
28	19139	19149	$A'\,(2) + \nu_1 + \nu_2$
2	19280	19275	$A'\,(1) + 2\nu_0 + \nu_1 + \nu_2$
2	19383	19389	$A'\,(1) + \nu_1 + \nu_2 + \nu_3$
85	19590	19585	$A'\,(1) + 2\nu_1$
18	19735	19741	$A'\,(1) + 2\nu_0 + 2\nu_1$
20	19867	19887	$A'\,(1) + 2\nu_1 + \nu_2$
22	19912	19917	$A'\,(2) + 2\nu_1 + \nu_2$
1	20165	20157	$A'\,(1) + 2\nu_1 + \nu_2 + \nu_3$
50	20350	20353	$A'\,(1) + 3\nu_1$
12	20635	20655	$A'\,(1) + 3\nu_1 + \nu_2$
12	20692	20685	$A'\,(2) + 3\nu_1 + \nu_2$
0.5	20932	20925	$A'\,(1) + 3\nu_1 + \nu_2 + \nu_3$
19	21131	21121	$A'\,(1) + 4\nu_1$
4	21448	21423	$A'\,(1) + 4\nu_1 + \nu_2$
9	21885	21889	$A'\,(1) + 5\nu_1$
7	22650	22657	$A'\,(1) + 6\nu_1$

Results of Analysis

$\parallel a$	$A'\,(1)$	$18051\ \mathrm{cm}^{-1}$	$\nu_1 = 768\ \mathrm{cm}^{-1}$
	$A'\,(2)$	$18076\ \mathrm{cm}^{-1}$	$\nu_2 = 325\ \mathrm{cm}^{-1}$
			$\nu_3 = 280\ \mathrm{cm}^{-1}$
			$\nu_0 = 78\ \mathrm{cm}^{-1}$
$\parallel b$	A''	$18043\ \mathrm{cm}^{-1}$	$\nu_1 = 768\ \mathrm{cm}^{-1}$
			$\nu_2 = 302\ \mathrm{cm}^{-1}$
			$\nu_3 = 255\ \mathrm{cm}^{-1}$
			$\nu_0 = 78\ \mathrm{cm}^{-1}$
$\parallel c$	$A'\,(1)$	$18049\ \mathrm{cm}^{-1}$	$\nu_1 = 768\ \mathrm{cm}^{-1}$
	$A'\,(2)$	$18079\ \mathrm{cm}^{-1}$	$\nu_2 = 302\ \mathrm{cm}^{-1}$
			$\nu_3 = 270\ \mathrm{cm}^{-1}$

It should also be pointed out that the position of the electronic origin of the band is dependent upon the concentration of $KMnO_4$ in $KClO_4$. Teltow found that the absorption edge of pure $KMnO_4$ is displaced 430 cm^{-1} towards the red when compared with the $KClO_4$ crystals containing 3 mol-% $KMnO_4$.

If MnO_4^- is put into other host lattices the bands also shift around some few hundred wavenumbers. These shifts are undoubtedly connected with the energy of interaction of the charge distribution of an excited molecule with that of the host lattice [*8*].

Of the vibrational frequencies which occur $\nu_0 = 78\ \mathrm{cm}^{-1}$ is undoubtedly a lattice vibration, and $\nu_1 = 768\ \mathrm{cm}^{-1}$ the totally symmetric stretching frequency of the MnO_4^- complex in the excited state. ν_2 and ν_3 must be other totally symmetric frequencies of the complex in the C_s symmetry. In T_d symmetry vibrational frequencies of a_1, e, t_2 and t_2 symmetry would occur, and in C_s symmetry both e and t_2 give split components which in the lower symmetry transform like a'.

No complete analysis of the vibrational frequencies of MnO_4^- in its ground state has yet been performed. Using the measurements of Miller et al. [9] we tentatively assign $\nu_3\ (t_2)$ to $850\ \mathrm{cm}^{-1}$ and $\nu_4\ (t_2)$ to $390\ \mathrm{cm}^{-1}$. For the isoelectronic ion CrO_4^{2-} Stammreich et al. [13] found $\nu_1\ (a_1) = 847\ \mathrm{cm}^{-1}$, $\nu_2\ (e) = 348\ \mathrm{cm}^{-1}$, $\nu_3\ (t_2) = 884\ \mathrm{cm}^{-1}$ and $\nu_4\ (t_2) = 368\ \mathrm{cm}^{-1}$. The values for $\nu_3\ (t_2)$ and $\nu_4\ (t_2)$ in MnO_4^- and CrO_4^{2-} are seen to agree rather well, and we shall therefore in MnO_4^- assume* $\nu_2\ (e) = 350\ \mathrm{cm}^{-1}$ and $\nu_1\ (a_1) = 850\ \mathrm{cm}^{-1}$.

The totally symmetric vibrational frequency ν_1 is thus diminished $\sim 10\%$ in the excited state. The a' components of the e and t_2 vibrational frequencies are supposed to undergo a similar reduction, and since $\nu_4\ (t_2)$ produces two a' and $\nu_2\ (e)$ one a' we would expect to see three other vibrational frequencies around $300\ \mathrm{cm}^{-1}$. So far the accuracy of the data goes (Tab. 1) the evidence certainly points in that way. On the other hand the two a' components of $\nu_3\ (t_2)$ should have values around $800\ \mathrm{cm}^{-1}$. However, from the data they cannot be distinguished from the $\nu_1\ (a')$ vibrational frequency.

The longer progression is seen to be in ν_1, e.g. for A' (1) eight quanta are observed. This indicates that the bond distance Mn-O is greater in the excited state than in the ground state. Assuming that we are dealing with harmonic vibrations, and taking the vibrational frequency to be the same in the ground and excited state, we find (see Appendix) calling the intensity of the $0 \rightarrow n$ vibrational band for I_n

$$I_n = \frac{k}{n} I_{n-1}$$

with $k = \frac{1}{2} (\Delta r)^2 \alpha;\ \alpha = \frac{4\pi^2 \nu c m}{h}$.

For the above mentioned progression we get with $\nu_1 = 768\ \mathrm{cm}^{-1}$ and $k = 1.73$ (see Tab. 2) $\Delta r \approx 0.10$ Å. In the ground state the Mn-O bond length is some [10]

Table 2. *Intensity distribution for the progression $A' \rightarrow A'$ (1) $+ n\nu_1$ with $\nu_1 = 768\ cm^{-1}$*

Frequency and assignment	Measured relative intensity	k	Calculated relative intensity taking k = 1.73
18051; $0 \leftarrow 0$	55	—	—
18821; $1 \leftarrow 0$	100	1.82	95
19592; $2 \leftarrow 0$	80	1.60	82
20352; $3 \leftarrow 0$	50	1.87	47
21125; $4 \leftarrow 0$	19	1.52	20
21881; $5 \leftarrow 0$	7	1.83	7
22632; $6 \leftarrow 0$	3	(2.57)	2
23396; $7 \leftarrow 0$	1	(2.33)	0.5
24160; $8 \leftarrow 0$	0.3	(2.68)	—

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* A calculation using a valence force potential [7] taking $\nu_3\ (t_2) = 850\ \mathrm{cm}^{-1}$ and $\nu_4\ (t_2) = 390\ \mathrm{cm}^{-1}$ yields $\nu_2\ (e) = 390\ \mathrm{cm}^{-1}$ and $\nu_1\ (a_1) = 765\ \mathrm{cm}^{-1}$.

1.60 Å. The intensity distribution then gives a bond distance *Mn-O* equal to $\sim$ 1.70 Å in the first $^1T_2$ state.

The above estimate is of course only an order of magnitude calculation. However, from the analysis of the vibrational intensity distribution it seems likely that the molecule is a great deal more expanded than bent in the first excited $^1T_2$ state.

Second $^1A_1 \rightarrow {}^1T_2$ Band

The second very broad band shows up in the solution spectrum of MnO_4^- at 32000 cm^{-1}. The oscillator strength is $f \approx 0.07$. This band is likewise assigned as an orbital allowed $^1A_1 \rightarrow {}^1T_2$ transition. The state is supposed to arise from a $t_1 \rightarrow t_2$ electron excitation [*4*, *2*].

TELTOW's measurements of this band $\perp$ c in $KClO_4$ only show a bit of fine structure and a progression in single quanta with a frequency of 760 cm^{-1}. The first bands are doublets, and split by some 170 cm^{-1}. We take this splitting to be the site group splitting of the second $^1A_1 \rightarrow {}^1T_2$ band, and place the electronic origin at 30723 cm^{-1}.

The progression in ν_1 has its highest intensity in the fourth member of the series, and by fitting the relative intensities in the same way as for the first $^1A_1 \rightarrow {}^1T_2$ band we find that the bond distance *Mn-O* is 0.14 Å greater in this state than for the ground state.

The "forbidden" Transitions

The promotion of a t_1 electron to an e orbital produces states of symmetry $^1T_1$, $^3T_2$ and $^3T_1$ beside the "first" $^1T_2$ state. A simplified calculation (Appendix II) gives the order $E\,(^1T_2) > E\,(^1T_1) > E\,(^3T_1) \approx E\,(^3T_2)$. We should in other words expect weak transitions on the red side of the first $^1A_1 \rightarrow {}^1T_2$ transition. Such transitions were also observed by TELTOW.

With the electric vector parallel to the b axis, $KMnO_4$ dissolved in $KClO_4$ shows a sharp line at 14446 cm^{-1} followed by a weak progression. Nothing like this is observed [*15*] with the electric vector parallel to a or c. Similarly in $LiClO_4 \cdot 3\,H_2O$ a sharp line is observed at 13767 cm^{-1} with the electric vector $\perp$ c. The shift of 679 cm^{-1} between these two lines is taken to be due to interactions between the MnO_4^- unit and the host lattice; at least the order of magnitude of the shift is the same here as was found for the $^1A_1 \rightarrow {}^1T_2$ transition in the same two lattices.

TELTOW [*15*] points out that the direction in which the sharp line is observed always is perpendicular to the main symmetry element of the distorted MnO_4^- tetrahedron. With $LiClO_4 \cdot 3\,H_2O$ possessing the site group symmetry C_{3v} a T_1 state would split into an E and A_2 state. The c axis is the three-fold axis of the trigonal MnO_4^- unit. Therefore we would expect the transition $^1A_1 \rightarrow {}^1E$ to be polarized $\perp$ c, and the $^1A_1 \rightarrow {}^1A_2$ transition to be orbitally forbidden. The $^1A_1 \rightarrow {}^1E$ transition is of course only made "allowed" by configuration interaction with the $^1E\,(^1T_2)$ state. Since such a behaviour is exactly what is observed, it seems reasonable to assign the line which in $LiClO_4$ is observed at 13767 cm^{-1} to the vibrationless transition $^1A_1 \rightarrow {}^1E\,(T_1)$.

It seems, therefore, natural to assume that the absorption lines which in $KClO_4$ start at 14446 cm^{-1} mark the beginning of the $^1T_1$ state. Yet such an assumption presents some difficulties. In the C_s site group symmetry T_1 should split into two A'' states (polarized $\|$ b) and one A' state (polarized $\|$ a and $\|$ c). *Assuming* that all the three $0 \rightarrow 0$ bands should possess intensities of equal magnitude we would then expect to see not a single sharp line parallel to b, but a doublet. Furthermore with the electric vector parallel to a we would expect to see another intense line.

The fact that only one intense line is observed parallel to b led WOLFSBERG and HELMHOLZ to assign this transition to an $^1A' \rightarrow {}^1A''$ (E) transition. However, such an assignment likewise fails to account for the missing A' (E) state. Indeed, in order to account for the band structure WOLFSBERG and HELMHOLZ [*16*] were led to postulate that the $0 \rightarrow 0$ transitions to states of A' symmetry had zero intensity. However, if we look at TELTOW's picture in Ref. 14, p. 420, we notice that parallel to b strong doublets are observed in the *middle of the band* at 15246 and 15324 cm^{-1} and at 16049 and 16117 cm^{-1}. The doublet splitting is seen to be 78 cm^{-1} and 68 cm^{-1} respectively. Furthermore, a line of moderate intensity is found at 14526 cm^{-1} (see Ref. [*15*], p. 202) 80 cm^{-1} above the sharp line at 14446 cm^{-1}. The overall separation between the doublets is 800 cm^{-1}. Therefore, giving up the preconceived idea that the *first* doublet should possess equal intensity, we assign the lines at 14446 cm^{-1} and 14526 cm^{-1} as the two vibrationless transitions $^1A \rightarrow {}^1A''$ (1) and $^1A''$ (2). A vibrational progression in ν_1 (a_1), with ν_1 equal to 800 cm^{-1} then accounts for the dominating "doublet" lines in the spectrum parallel to b.

The $^1A' \rightarrow {}^1A'$ (T_1) transition should be seen polarized in the a and c directions. The first weak line occurs $\|$ a at 14567 cm^{-1} and $\|$ c at 14605 cm^{-1}. The separation is 38 cm^{-1}, but since TELTOW's halfwidths are respectively 90 cm^{-1} and 65 cm^{-1}, the uncertainty is well inside the experimental error. We take this line to be the transition to $^1A'$. Progressions with a separation of $\sim$ 800 cm^{-1} are again seen in both polarizations; a great deal of lattice vibrations seem likewise to be excited.

If finally we look at TELTOW's measurements of MnO_4^- in $NaClO_4$, the absorption lines seen $\|$ b and $\|$ c (see WOLFSBERG and HELMHOLZ [*16*] for the reversals of a and b) start much further toward the red than do the absorption bands $\|$ a. The site group symmetry of $NaClO_4$ is C_{2v}, that is a T_1 state is split into three substates; A_2, B_1 and B_2. Transitions to B_1 and B_2 are polarized, respectively, along b and c. The $A_1 \rightarrow A_2$ transition is orbitally forbidden.

The first lines occur $\|$ b and $\|$ c at some 13125 cm^{-1}, the first observed line $\|$ a at some 15370 cm^{-1}. A splitting of this order of magnitude seems too large for a single state. We therefore propose that the absorption below and around 14000 cm^{-1} is due to the presence of one or both of $^3T_1$ and $^3T_2$. With the nearest state being a $^1T_1$ (A_2, B_1 and B_2 in C_{2v}) we see, assuming this to be the state from which the spinforbidden transitions "steal" their intensity, that the polarizations agree with the experiments.

Furthermore, with the progressions of the triplet state(s) stretching into the region of the $^1T_1$ state it is small wonder that this region of the spectrum is highly irregular and difficult to sort out.

Weak lines are also located between the "first" and "second" ${}^1A_1 \rightarrow {}^1T_2$ band. However, the details are not sufficient to allow an analysis. With the orbital assignments of Ballhausen and Liehr [2] we should expect both singlets and triplets of symmetry A_2, E and T_1 and a triplet of symmetry T_2 to occur here.

All in all it seems doubtful that the weak bands have been measured with sufficiently high accuracy to allow for a detailed analysis. Apart from the above suggestions as to the nature of the "forbidden" transitions no further analysis will therefore be attempted. However, in conclusion we feel confident that the available experimental facts can be rationalized using the Ballhausen and Liehr scheme.

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Appendix 1

The intensity ratio of the transitions from the vibrational ground state 0 in the electronic state A with vibrational frequency ν' to the vibrational states 0 and n in the electronic state B with vibrational frequency ν is given by [6]

$$\frac{I\,(Bn \leftarrow A0)}{I\,(B0 \leftarrow A0)} = \frac{I_n}{I_0} = \left[\frac{\int \psi_0\,(r, \alpha')\,\psi_n\,(r + \Delta r, \alpha)\,d\tau}{\int \psi_0\,(r, \alpha')\,\psi_0\,(r + \Delta r, \alpha)\,d\tau}\right]^2$$

where ψ_n is the wavefunction for the harmonic oscillator as given e.g. in Pauling and Wilson [11].

$$\psi_n\,(r, \alpha) = N_n e^{-\frac{1}{2}\alpha r^2}\,H_n\,(\sqrt{\alpha}\,r)$$

$H_n\,(x)$ are the Hermite polynomials and

$$\alpha = \frac{4\pi^2\,m\,\nu\,c}{h} \quad \text{with } N_n = \sqrt{\sqrt{\frac{\alpha}{\pi}}\,\frac{1}{2^n n!}}\,.$$

ν is measured in cm^{-1}.

From the general addition formula for the Hermite polynomials, given for instance in the Bateman Manuscript [3], we get the expansion

$$H_n\left(\frac{a_1}{\sqrt{a_1^2 + a_2^2}}\,x_1 + \frac{a_2}{\sqrt{a_1^2 + a_2^2}}\,x_2\right) = \left(\frac{a_2}{\sqrt{a_1^2 + a_2^2}}\right)^n H_0\,(x_1)\,H_n\,(x_2)$$
$$+ \text{ higher terms in } H_n\,(x_1).$$

Using this formula to expand $H_n\,(r + \Delta r)$ and utilizing the orthogonality of the harmonic oscillator wavefunctions one obtains

$$\frac{I_n}{I_0} = \frac{1}{2^n n!}\left(\frac{\alpha' - \alpha}{\alpha + \alpha'}\right)^n \left\{H_n\left(\Delta r\sqrt{\frac{\alpha\,(\alpha + \alpha')}{\alpha' - \alpha}}\;\frac{\alpha'}{\alpha + \alpha'}\right)\right\}^2$$

In the case $\alpha' = \alpha$, that is with the vibrational frequency being the same in the two states, the above expression reduces to

$$I_n = \left[\frac{1}{2}\,\alpha\,(\Delta r)^2\right]^n \frac{1}{n!}\,I_0$$

Calling $\frac{1}{2}\,\alpha\,(\Delta r)^2 = k$ we find

$$I_n = \frac{k}{n}\,I_{n-1}$$

Small differences in the vibrational frequencies are usually not of importance and the latter formula is therefore by far the most easy to use.

Appendix 2

Using the linear combinations for the various π orbitals given for instance in Ref. 2 we can write down single determinental wavefunctions disregarding the electrons in the closed shells below the t_1 orbital. Assuming t_1 to be a pure ligand π-orbital and $e^a(\pi)$ to be of the form $\psi(e^a\pi) = \sqrt{1-\lambda^2}\,(e) - \lambda\,(\pi)$ we get, retaining only one-center integrals,

$$E(^1T_2) - E(^1T_1) = \frac{\lambda^2}{4}(A + B - 2C)$$

$$E(^1T_2) - E(^3T_2) = \frac{\lambda^2}{4}(2A)$$

$$E(^1T_2) - E(^3T_1) = \frac{\lambda^2}{4}(A + B)$$

with

$$A = (p_x p_x | \frac{1}{r_{12}} | p_x p_x)$$

$$B = (p_x p_y | \frac{1}{r_{12}} | p_x p_y)$$

$$C = (p_x p_y | \frac{1}{r_{12}} | p_y p_x).$$

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