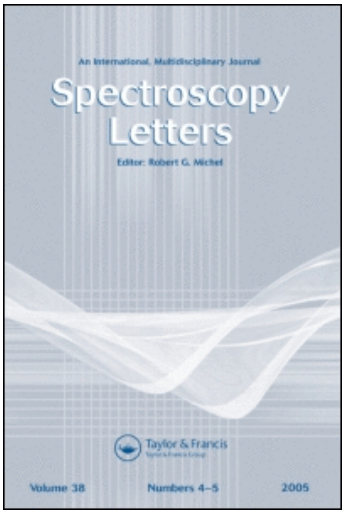

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Computer Resolution and Franck-Condon Analysis of the Electronic Absorption Spectrum of $KMnO_4$ in Water

Józef Myrczek[a]
[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wrocław, POLAND

To cite this Article Myrczek, Józef(1987) 'Computer Resolution and Franck-Condon Analysis of the Electronic Absorption Spectrum of $KMnO_4$ in Water', Spectroscopy Letters, 20: 12, 927 — 944
To link to this Article: DOI: 10.1080/00387018708081600
URL: http://dx.doi.org/10.1080/00387018708081600

SPECTROSCOPY LETTERS, 20(12), 927-944 (1987)

COMPUTER RESOLUTION AND FRANCK-CONDON ANALYSIS OF THE ELECTRONIC ABSORPTION SPECTRUM OF $KMnO_4$ IN WATER

key words: electronic spectroscopy, vibronic spectra, permanganate ion, Franck-Condon analysis, computer resolution of spectra

Józef Myrczek

Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, POLAND.

ABSTRACT

The electronic absorption spectrum of $KMnO_4$ in water solution was analyzed. The spectral contour was resolved into component bands and then Franck-Condon approach was applied. In the investigated range of 13000-48000 cm^{-1} a presence of three structureless and of two vibronic strong bands was stated. The change in the Mn-O equilibrium bond length was found to be 10.5pm for $2e \leftarrow 1t_1$ transition (vibronic band about 18000cm^{-1}) and to be 16pm for the $2e \leftarrow 3t_2$ transition (vibronic band about 30000cm^{-1}). The appropriate wavenumber of the vibrational mode in these excited electronic states was found to be 735cm^{-1} and about 780cm^{-1}, respectively. The ground electronic state wavenumber of the totally

symmetric vibrational mode was fitted to be equal to $828cm^{-1}$. Details of the proposed method of computer elaboration of electronic spectra with vibrational structure were discussed.

Electronic absorption spectra of some inorganic compounds consist of a number of strongly overlapped bands due to their vibronic structure.[1-5] A detailed analysis of spectral contours of such compounds provides some useful information about their structure in both ground and excited electronic states.

The electronic spectrum of permanganate ion is the typical example of vibronic spectra.[1] The main part of the past works based on the analysis of permanganate ion spectra in low temperatures and different polarizations. In such conditions the vibronic structure is rather good resolved and can be effectively studied.[1,3,6] Spectra of solutions as a rule are relatively poor resolved so their analysis has to be more sophisticated.

The main purpose of this work is a presentation of a new computer method for an effective study of vibronic spectra of solutions. This method has been applied to the electronic absorption spectrum of $KMnO_4$ in water. The method allowed us to fit the geometric parameters of spectral contour, to establish the origins and parameters of two progressions in the UV/VIS range as well as to calculate the changes in the Mn-O equilibrium bond lengths and vibrational energy resulting from the electronic excitations of the soluted permanganate ion.

EXPERIMENTAL

The electronic absorption spectrum of 0.0003M $KMnO_4$ in water solution was recorded at room temperature with a Hitachi 356 UV/VIS spectrophotometer connected with a system CAMAC. The investigated range was 13000-48000cm^{-1}. The distances between experimental points were generally taken to be equal to 50cm^{-1}, but in the most important ranges they were taken to be 20 and 10 cm^{-1}. All the calculations were performed on an IBM PC/XT microcomputer.

THEORY AND MODE OF CALCULATION

A spectral contour was treated as a sum of symmetrical (structureless) and vibronic bands. The vibronic structure in electronic absorption band is mainly due to progression which corresponds to a set of transitions from the given vibrational state of the ground electronic state to the succesive vibrational states of the excited electronic state.(At low and room temperature the main progression consists of transitions from the lowest vibrational state of the ground electronic state.) In our approach every vibronic band was treated as a progression described by a sum of vibrational members. Spectral contours of the component symmetrical bands are given by a mixed Guassian-Lorentzian function Eq.1.

$$F(x(i))=EXT\ [R* 2^{-z^2} + (1-R)/(1+z^2)] \qquad (1)$$

where $z=(x(i)-x_o)/WDT$, $x(i)$ is the wavenumber of the i-th measured point, x_o - the peak position of the band, EXT - the maximum intensity of this band and WDT is its half-width. R is the proportion of the Gaussian

function in the theoretical bandshape and 1-R is the proportion of the Lorentzian function in the bandshape.

The necessary calculations were connected with two main resolutions of the whole spectral contour into the component vibronic and structureless bands and Franck-Condon analysis.

The iterative procedure for resolution of the electronic absorption spectrum based on the least-squares-method. A procedure convergence measure was defined by the root-mean-square deviation RMS given by Eq.2..[7]

$$RMS = 100/Y_{max} * \sqrt{\sum_{i=1}^{NP} [F_t(i) - Y(i)]^2/NP} \quad [\%] \qquad (2)$$

F_t is a theoretical spectral contour, Y(i) - experimental intensity at the point x(i), Y_{max}- maximum intensity in the investigated range, NP - a number of the measured points.

The First Resolution

The fundamental idea of this resolution was the use of a complete mathematical description of the whole spectrum contour including relationships between component members of the progression. Once these relationships are established the progression contour may be treated as a unit during the resolution. This approach was discussed in details in our previous work.[7]

We took into consideration the following relations between component members of the same progression:

A. The positions of the member transitions of a progression may be expressed by an anharmonic oscillator approximation (Eq.3).

$$E_{n\leftarrow o} = E_{o\leftarrow o} + n\,\omega_o - n(n+1)\omega_o x_o \qquad (3)$$

$E_{n\leftarrow o}$ is the energy of the transition between the lowest vibrational state of the ground electronic state and the vibrational state n of the excited electronic state.

B. The halfwidth of bands is the same for all members.

C. The relation between the intensities of the progression members is described by the Poisson distribution (Eq.4.).

$$I_{n\leftarrow o} = I_{o\leftarrow o} * k^n / n! \qquad (4)$$

This relation was derived by Ballhausen.[1] He assumed the harmonic vibrations and took the vibrational frequency (ν) to be the same in the ground and excited electronic states. Finally he obtained the Eq.4. where $k = 2.0\,(\Delta r)^2\,\pi^2\,\nu\,c\,m / h$. Δr is the displacement between the bond length Mn-O in the ground and excited electronic states (normal coordinate).

The regression analysis of intensities of at least three succesive progression members according to Eq.5. (derived from Eq.4.) allowed us to estimate the origin of the progression even if there was impossible to find it visually from the spectral contour.

$$I_{n-1\leftarrow o} / I_{n\leftarrow o} = n * 1/k \qquad (5)$$

The resolution of the spectra including relations A-C gives reasonable results although the final fitting to the experimental spectrum is not very good as these relations are not exactly fulfilled.[7]

The Second Resolution

In this resolution the relations A-C were neglected and every progression member was fitted in an

independent way. The initial parameters corresponded to the final parameters of the first resolution. In effect the second resolution was good convergent even in the case of strongly overlapped bands and the geometric parameters of the component bands were fitted exactly.

The Franck-Condon Analysis

Some authors described approximate methods for applying the Franck-Condon principle.[1,2,8,9,10] The most popular method[1] neglects the difference in the frequencies between the ground and excited states. This approach results in the previously used Eq.4. In our work we chose more adequate method[2] convenient for transition metal complexes. Relations which are necessary for numerical computation of absorption spectra are given below (Eq.6,7,8.). The vibrational overlap integrals $R_{n,o}$ have been evaluated for harmonic oscillator wavefunctions.

$$I_{n<-o} \;/\; I_{o<-o} = (E_{n<-o} \;/\; E_{o<-o}) * (R_{n,o}/R_{o,o})^2 \qquad (6)$$

$$R_{o,o} = [\; 2*\delta \;/\; (1+\delta^2)^{1/2} \;] * \exp(-0.5*\rho^2) \qquad (7)$$

$$R_{n+1,o} = \frac{-2*\delta*D*R_{n,o} - (2n)^{1/2} * (\delta^2-1)*R_{n-1,o}}{(\delta^2 + 1)\;[2(n+1)]^{1/2}} \qquad (8)$$

$$\delta=(\nu_o'/\nu_o'')^{1/2} \qquad D=C*\Delta S*(m*\nu_o')^{1/2}\;,\quad \rho=D/(1+\delta^2)^{1/2},$$

ΔS is the displacement of the minimum of the potential surface of the excited states along the stretching normal coordinate in $\mathring{A}$, ν_o'' and ν_o' are the ground and excited electronic state fundamental wavenumbers(cm^{-1}),

m is the reduced mass (from the G matrix) in amu's, constant C=0.1722 (see Ref.11. p.181, this constant was cited erroneosly in original Ref.2).

The elaborated computer program based on simplex procedure described by O'Neill.[12] The program matches values of ΔS and ν_o'. The values of intensity and position of progression members as well as the value of ν_o' were obtained from resolved spectra. A measure of fit was defined by the Eq.9.

$$\sigma = \sqrt{\sum \left[\left(I^{exp}_{n\leftarrow o} / I^{theor}_{n\leftarrow o} \right) - 1 \right]^2 / M} \qquad (9)$$

M is the number of investigated progression members.

RESULTS AND DISCUSSION

The electronic spectrum of permanganate ion has been a subject of intensive study since the early experimental work of Teltow[13,14] and theoretical consideration of Wolfsberg and Helmholz[15] and Ballhausen.[1,16] The main topic of discussions was connected with the proper level scheme and assignment of theoretical bands to theoretically anticipated transitions. Nowadays the accepted scheme of electronic excitement of MnO_4^- ion is as follows[11] (the only electric dipole allowed transitions are the $^1T_2 \leftarrow\!\!- \; ^1A_1$ transitions, they are shown bold):

ground configuration: $(3t_2)^6(1t_1)^6$

excited configuration	states
$(3t_2)^6(1t_1)^5(2e)$	$^3T_1 + {}^3T_2 + {}^1T_1 + {}^1T_2$

$(3t_2)^6(1t_1)^5(4t_2)$	$^3A_2 + {}^3E + {}^3T_1 + {}^3T_2$ $^1A_2 + {}^1E + {}^1T_1 + {}^1T_2$
$(3t_2)^5(1t_1)^6(2e)$	$^3T_1 + {}^3T_2 + {}^1T_1 + {}^1T_2$
$(3t_2)^5(1t_1)^6(4t_2)$	$^3A_1 + {}^3E + {}^3T_1 + {}^3T_2$ $^1A_1 + {}^1E + {}^1T_1 + {}^1T_2$

Resolutions of spectral contour

The level scheme and the earlier assignments of the electronic transitions in the low temperature spectra of permanganate ion[3] allowed us to establish the proper interpretation of the results of the first and second resolutions (Tab.1. and 2.). The resolved spectrum is displayed in Fig.1. The progression members are represented by their maximum intensities only in this figure. The bands with maximum intensities below 10 $dm^3/mol*cm$ were neglected .

Our results are in good agreement with the published data obtained from solid state, low temperature and polarizable light spectra (see Table 3.).

The serious problem of the proper assignments of the results of our resolutions was connected with the origin of the second progression. According to the work of Ballhausen[1] it was found to be equal to 30723 cm^{-1} for $KMnO_4$ dissolved in $KClO_4$ at 20K. However from our calculations it was found that it should be 29250 cm^{-1}. The additional calculations checked our results. The calculation consisted of four complete analyses of the spectrum in the range 24000-37000cm^{-1} for the following wavenumbers of progression origin (at a distance of approximate wavenumber of vibration): about 28500 cm^{-1},

TABLE 1

Results of the First Resolution of the Electronic Absorption Spectrum of $KMnO_4$ in Water. RMS=0.66%.

Structureless bands:					
No	EXT $\frac{dm^3}{mol\ cm}$	X_o cm^{-1}	WDT/2 cm^{-1}	Assignment	Term
1.	254	16750	1558	$2e<-1t_1$	$^1T_1$
2.	210	21182	1685	$2e<-1t_1$	$^3T_2$
3.	1285	29251	2631	$4t_2<-1t_1$	$^1T_2$
4.	1821	45121	4792	$4t_2<-3t_2$	$^1T_2$
5.	13744	53394	3052	out of range	

Progressions:								
No	$I_{o<-o}$ $\frac{dm^3}{mol\ cm}$	k	$E_{o<-o}$ cm^{-1}	ω_o cm^{-1}	$\omega_o x_o$ cm^{-1}	WDT/2 cm^{-1}	Assignment	Term
1.	901	2.1	17620	736	2	358	$2e<-1t_1$	$^1T_2$
2.	28	5.5	29255	762	4	391	$2e<-3t_2$	$^1T_2$

about 29250 cm^{-1}, about 30000 cm^{-1} and about 30700 cm^{-1}. These possibilities cover the whole reasonable range of the second progression origin. A plot of the values of the fitting measures RMS and σ against the proposed values of the wavenumber of progression origin is shown in Fig.2. The obtained results confirmed our assignment. The first member of the second progression has a very low intensity and it would be very difficult to detect it without detailed computer analysis.

Only two allowed bands of water solution spectrum were structured enough to be treated as vibronic bands

TABLE 2

Results of the Second Resolution of the Electronic Absorption Spectrum of $KMnO_4$ in Water. RMS=0.18%.

No	EXT $\frac{dm^3}{mol\ cm}$	X_o cm^{-1}	WDT/2 cm^{-1}	Assignment	Term (vibronic member)
1.	240	17055	1872	$2e \leftarrow 1t_1$	$^1T_1$
2.	52	18900	1749	$2e \leftarrow 1t_1$	$^3T_2$
3.	1260	29001	2426	$4t_2 \leftarrow 1t_1$	$^1T_2$
4.	1751	44778	4616	$4t_2 \leftarrow 3t_2$	$^1T_2$
5.	9723	53284	3330	out of range	
First progression:				$2e \leftarrow 1t_1$	$^1T_2$
6.	976	17612	309		0-0
7.	1971	18345	335		1-0
8.	2072	19075	343		2-0
9.	1557	19801	359		3-0
10.	919	20527	369		4-0
11.	485	21247	389		5-0
12.	216	21939	390		6-0
13.	140	22615	503		7-0
14.	67	23430	495		8-0
15.	30	24180	506		9-0
Second progression				$2e \leftarrow 3t_2$	$^1T_2$
16.	15	29039	211		0-0
17.	200	29972	456		1-0
18.	515	30742	424		2-0
19.	869	31487	419		3-0
20.	1101	32227	425		4-0
21.	1127	32954	433		5-0
22.	975	33665	441		6-0
23.	732	34364	446		7-0
24.	496	35052	445		8-0
25.	305	35727	440		9-0
26.	172	36393	432		10-0
27.	91	37042	419		11-0
28.	44	37693	405		12-0
29.	13	38363	329		13-0

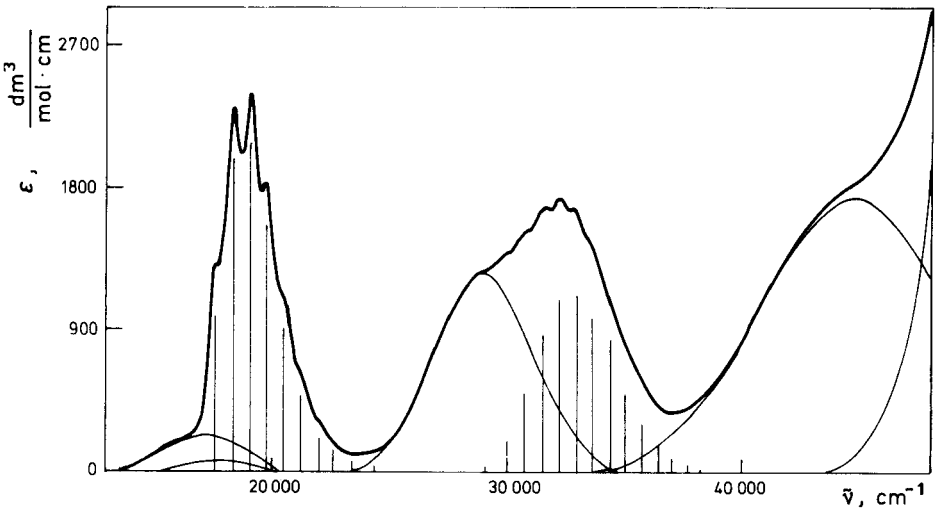

FIG.1. Resolution of the vibronic spectrum of $KMnO_4$ in water solution.

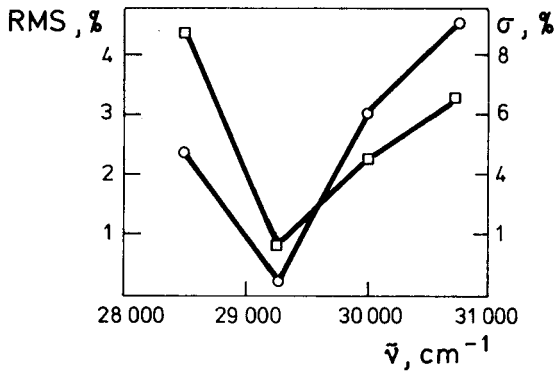

FIG.2. A plot of the fitting measures against the proposed wavenumbers of the origin of the second progression. □ - RMS, ○ - σ.

in our analysis. Other bands were treated as structureless and their maximum intensities were calculated only. Some published data provide transition origins but not their maximum intensity positions (see Tab.3.).

Generally the differences of the transition energies from literature data and from our calculations are small and can be explained by the differences in the measurement conditions (state, temperature, concentration). In our analysis we did not find the forbidden band about 25000cm^{-1}. We suppose that it was too weak therefore was neglected during the analysis

The position of the origin of the second progression is given by an approximated value as the first progression member was very weak so its position could not be fitted very exactly.

Franck-Condon analysis

Franck-Condon analysis was performed for well structured bands only. We took into consideration the intensive progression members with maximum intensities higher than 500 dm^3/mol*cm as their parameters were fitted more exactly during the resolutions. For the totally symmetric vibration mode of $[MnO_4]^-$ *m* is equal to 16 amu. The parameter values leading to the best fitting (according to Eq.9.) are given in Table 4, where they are compared with literature data. Values of $E_{o<-o}$ and ν_o' were estimated from the results of the resolutions , parameters ν_o'' and ΔS were fitted by simplex procedure. For the first progression we obtained σ=0.4%, for the second progression σ=0.2%.

Totally symmetric mode in the ground state of crystal $KMnO_4$ is equal to 844cm^{-1},[18] so our fitted

TABLE 3

Energies of the Progression Origins and Bands Maximum Intensities in the Electronic Absorption Spectra of Permanganate Ion. All Data in cm^{-1}.

Excited Term		Literature data (1)[a]	(3)[b]	(6)[c]	(17)[d]	This work
$^1T_1$	origin	14446	15000		13774[f]	
	maximum					17055
$^1T_2$	origin	18050	17646	18072	17634[e] 18182[f]	17612
	maximum	18821	19242[g]	18842	18409[e] 18947[f]	19075
$^3T_2$	origin		17920			
	maximum					18900
$^1T_1$	origin		24661		24938[f]	
$^1T_2$	origin	30723	30230		30221[e] 30675[f]	~29250
	maximum		32415[g]	33000	32436[e] 32895[f]	32954
$^1T_2$	maximum		29500			29001
$^1T_2$	maximum		44450	43500	43500	44778

[a] $KMnO_4$ in $KClO_4$, 20K; [b] $(C_2H_5)_4N[MnO_4]$ in KBr, 10K; [c] $KMnO_4/KClO_4$, 4.2K,20K; [d] $LiClO_4 \cdot 3H_2O/LiMnO_4 \cdot 3H_2O$, 4.2K [e] parallel polarization ; [f] perpendicular polarization; [g] estimated data from original figures.

TABLE 4

Parameters Obtained by the Franck-Condon Analysis of Vibronic Bands of $[MnO_4]^-$ Spectra.

No	$E_{o<-o}$ cm^{-1}	ν'_o cm^{-1}	ν''_o cm^{-1}	ΔS $\AA$	Reference
1.	17612	735	829	0.105	This work
	18051	768	768	0.10	(1)[a]
	17391	745	834	0.09	(10)[b]
	17950	740	846	0.092	(10)[c]
2.	~29250	782	828	0.16	This work
	30723	760	760	~0.14	(1)[a]

[a] $KMnO_4$ in $KClO_4$, 20K, absorption spectra.

[b] $[Ph_4P][MnO_4]$, Resonance Raman Excitation spectra

[c] $KMnO_4$ in $KClO_4$, Resonance Raman Excitation Spectra

values of ν'_o' are quite resonable. Moreover they are almost the same for both the first and the second progressions (the ground state is the same for both transitions). The values of ΔS are given in normal coordinates. The corresponding changes of the Mn-O distance are equal $\Delta S/2$. The obtained values are in good agreement with cited data. ΔS for the first progression is only a little higher than literature data. This fact is consistent with the spectra as in our spectral contour the most intensive member was 2<-0 meanwhile in the references it was 1<-0. However the intensities of the 2<-0 and 1<-0 members are very similar in both cases so the differences are small. Similarly the ΔS for the second progression is about 15% higher than that of Ballhausen.[1] In our water

solution spectrum the most intensive member was 5<-0 meanwhile it was presumed to be 2<-0 by Ballhausen [1] (see discussion connected with FIG.2.). The value of displacement ΔS for the second progression is about 50% higher than for the first progression.

We can assume that the displacements ΔS are connected with an increase in Mn-O bond length.[19] We can deduce that in the soluted permanganate ion the increase in Mn-O bond length is slightly higher in comparison with solid state.

Our results seem to be the first in the literature for the solution spectra. The Franck-Condon analysis of Ballhausen[1] was very simplified ($\nu_o' = \nu_o''$), the analysis of Clark and Stewart[10] was done only for the first progression by use of Resonance Raman Excitation profiles but not absorption spectra.

CONCLUSIONS

In this work we present a method of computer analysis of vibronic spectra which appears to be a convenient tool for analysis of solution spectra of complex compounds. The method includes careful resolutions of the spectra and then the Franck-Condon analysis based on the results of these resolutions.

The analysis of the electronic absorption spectrum of $KMnO_4$ in water at room temperature illustrates the usefulness of the method in determining the changes consequent on excitation from the ground to the excited electronic state. The presented analysis seem to be the first complete computer analysis of the permanganate ion absorption spectrum in solution. The obtained parameters can be compared with the results of analyses

provided by means of more sophisticated methods. This fact is the most important as it gives a chance to investigate changes which occur during dissolving of the molecule.

ACKNOWLEDGMENT

The author has benefitted greatly from discussion and guidance provided by Professor Adam Bartecki. Valued discussions with Dr. Maria Cieślak-Golonka are also acknowledged.

REFERENCES

1. Ballhausen C.J. A Vibrational Analysis of the MnO_4^- Bands. Theoret. Chim. Acta 1963; 1: 285-293.
2. Yersin H., Otto H., Zink J.I., Gliemann G. Franck-Condon Analysis of Transition-metal Complexes J. Am. Chem. Soc. 1980;102: 951-955.
3. Homborg H. Die Feinstruktur in den Schwingungs- und elektronischen Absorptionsspektren von $[CrO_4]^{2-}$ und $[MnO_4]^-$. Z. anorg. allg. Chem. 1983;498: 25-40.
4. Jeżowska-Trzebiatowska B., Bartecki A. Fine Structure of the Electronic Absorption Spectra of Uranyl Compounds. Spectrochim. Acta 1962; 18: 799-807.
5. Bersuker I.B. The Jahn-Teller Effect and Vibronic Interactions in Modern Chemistry, New York: Plenum Press, 1984, p.204-207.
6. Holt S.L., Ballhausen C.J. Low Temperature Spectra of $KMnO_4$ in $KClO_4$. Theor. Chim. Acta 1967; 7: 313-320.
7. Bartecki A., Myrczek J. Application of Computers to Vibronic Spectra. Comp. Enh. Spectr. 1984; 2: 53-60.
8. Henderson J.R., Muramoto M., Willett R.A. Harmonic Franck-Condon Overlap Integrals Including Displacement of Normal Coordinates. 1964; 41: 580-581.
9. Patterson H.H., Godfrey J.J., Kahn S.M. Sharp-Line Luminescence and Absorption Spectra of

the Tetrachloroplatinate(II) Ion Doped in Single Crystals of Cesium Hexachlorozirconate(IV) at $4^{o}K$. Inorg. Chem. 1972; 11: 2872-2878.

10. Clark R.J.H., Stewart B. Resonance Raman Excitation Profiles for the Permanganate Ion: Calculation of Franck-Condon Scattering Contributions for the Totally Symmetric Fundamental and Its Overtones and of the Equilibrium MnO Bond Length in the First $^{1}T_{2}$ Excited State. J. Am. Chem. Soc. 1981; 103: 6593-6599.

11. Lever A.B.P. Inorganic Electronic Spectroscopy, 2nd ed. Amsterdam, Oxford, New York: Elsevier, 1984.

12. O'Neill R. Function Minimization Using a Simplex Procedure. Appl. Statist. /J.R. Statist. Soc. C/ 1971; 20: 338-345.

13. Teltow J. Das Absorptionsspektrum des Permanganations in verschiedenen Kristallgittern. Z. Physik. Chem. Abt.B 1938; 40: 397-430.

14. Teltow J. Die Absorptionsspektren des Permanganat-, Chromat-, Vanadat- und Manganations in Kristallen. Z. Physik. Chem. Abt.B 1939; 43: 198-212.

15. Wolfsberg M., Helmholz L. The Spectra and Electronic Structure of the Tetrahedral Ions MnO_4^-, CrO_4^{2-} and ClO_4^-. J. Chem. Phys. 1952; 20:837-843.

16. Ballhausen C.J., Liehr A.D. Intensities in Inorganic Complexes. Part II. Tetrahedral Complexes. J. Mol. Struct. 1958; 2: 342-360.

17. Johnson L.W., McGlynn S.P. Electronic Absorption Spectrum of $LiMnO_4.3H_2O$ in $LiClO_4.3H_2O$. J. Chem. Phys. 1971; 55: 2985-2989.
Johnson L.W., Hughes E.,Jr., McGlynn S.P. Electronic Absorption Spectrum of MnO_4^- in the Far-Red Region. J. Chem. Phys. 1971; 55: 4476-4480.

18. Pinchas S., Samuel D., Petreanu E. The IR Absorption of 86% ^{18}O-potassium Permanganate. J. Inorg. Nucl. Chem. 1967; 29: 335-339.

19. Clark R.J.H., Dines T.J., Wolf M.L. Electronic and Resonance Raman Spectroscopic Studies on the Tetrathiomolybdate(VI) Ion, $[MoS_4]^{2-}$. J. Chem. Soc. Faraday Trans. II. 1982; 78:679-688.

Date Received: 08/13/87
Date Accepted: 09/22/87