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# Molecular Orbital Calculations on Transition Element Compounds

## IV. Effect of Electrostatic Environment of Crystal Lattices

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The Ewald method has been used to calculate the effect of electrostatic environments (crystal lattices) on the molecular orbitals and spectroscopic state levels of the oxyanions, permanganate and chromate. An estimate of factor group splitting based on a crude model suggests that it may be an observable effect in molecular ions in crystals. However the shifts in energy and the splitting of bands due to electrostatic effect of the lattice are predicted to be more important than the factor group splittings. Attention is drawn to the significant effect of the lattice field on the molecular orbital energies, making the uppermost filled orbital of the ground state strongly bonding, in contrast to the situation in the isolated anions.

Nach dem Verfahren von Ewald wurde der Einfluß des elektrostatischen Beitrages des Kristallgitters auf die MO's und spektroskopische Zustände des Permanganat- und Chromat-Anions berechnet. Eine rohe Abschätzung der Faktorgruppen-Aufspaltung legt die Vermutung nahe, daß auch dieser Effekt beobachtbar ist. Jedoch sind die Energieverschiebungen und Aufspaltungen infolge der Umgebung des Kristallgitters wahrscheinlich größer als die Faktorgruppen-Aufspaltung. Es wird besonders auf den bedeutenden Einfluß des Gitterfeldes auf die MO-Energien hingewiesen, die das oberste besetzte Orbital des Grundzustandes stark bindend machen, ganz im Gegensatz zur Situation für die isolierten Anionen.

La méthode d'Ewald a été utilisée pour calculer l'effet de l'environnement électrostatique (réseaux cristallins) sur les orbitales moléculaires et les états spectroscopiques des oxyanions permanganate et chromate. L'estimation de la séparation du groupe facteur sur la base d'un modèle grossier suggère que cet effet peut être observé dans les ions moléculaires dans les cristaux. Cependant les déplacements et les séparations des bandes dûs à l'effet électrostatique du réseau sont prédits comme étant plus grands que les séparations du groupe facteur. On attire l'attention sur l'effet significatif du champ du réseau sur les énergies des orbitales moléculaires, la plus haute orbitale occupée devenant fortement liante, contrairement à ce qui a lieu dans les anions isolés.

## Introduction

In the previous papers of this series [1–3] the CNDO and MCZDO molecular orbital methods have been used in calculations of the electronic structure and transition energies of isolated permanganate and chromate anions. Since the experimental data that have been compared with these calculations have been obtained either for solutions or for crystals, it is important to try to assess the effect of these environments on the calculated quantities. In this paper the effect of the crystal lattice is investigated. The main effect will be a change in electronic structure and transition energies caused by the potential due to the surrounding electrostatic charges of the other ions in the crystal.

In cases where the site symmetry of the ion on the crystal lattice is lower than the molecular symmetry, the free molecular ion transitions will be split in the crystal [4]. A further effect, probably much smaller than the last two and not as yet positively identified, is an exciton splitting of the transitions in cases where there is more than one molecular ion per unit cell.

The space group symmetry and lattice spacings are known for many ionic crystals containing the permanganate and chromate ions, but the actual atomic positions are known for very few. However, the latter are known for potassium permanganate [5], potassium chromate [6], and cesium chromate [7], and the space group symmetry for these is $D_{2h}^{16}$. There are four molecules per unit cell, the factor group being $D_{2h}$ and the site group $C_s$. Hence for the permanganate and chromate ions in these particular crystals, all molecular orbital and spectroscopic state degeneracy is removed, and all transitions are allowed. However, the lattice potential is small compared with the intramolecular potential and the distortion from $T_d$ symmetry will be slight. Thus the intensity of transitions arising from originally symmetry forbidden transitions under $T_d$ symmetry will be very weak. The allowed ${}^1T_2 \leftarrow {}^1A_1$ transition will be split into three transitions, two polarized in the crystal *ab* plane ($A'$ in $C_s$) and the other along the crystal *c* axis ($A''$ in $C_s$) with the crystal axes as defined by Lonsdale [8].

## Method

The effect of the electrostatic potential due to the surrounding charged atoms in the crystal lattice can be included as a perturbation ($V_{le}$) to the core Hamiltonian in the CNDO method used in previous papers [1, 2]. Then

$$H = T + V_{ne} + V_{le} \tag{1}$$

where $T$ is the kinetic energy operator, $V_{ne}$ the nucleus-eletron attraction operator and $V_{le}$ the crystal lattice-electron interaction operator. The core Hamiltonian matrix elements then become [4].

$$\alpha_\mu^l = \alpha_\mu^i + V_\mathrm{A}^l \tag{2}$$

$$(\beta_{\mu\mu}^\mathrm{AA})^l = (\beta_{\mu\mu}^\mathrm{AA})^i \tag{3}$$

$$\beta_{\mu\lambda}^\mathrm{AB} = (\beta_{\mu\lambda}^\mathrm{AB})^i + \tfrac{1}{2} S_{\mu\lambda}(V_\mathrm{A}^l + V_\mathrm{B}^l) \tag{4}$$

where the superscripts $i$ and $l$ represent the matrix elements of an isolated molecule and a molecule in the crystal environment respectively, and $V_\mathrm{A}^l$ represents the lattice potential at atom A. As the effects of adjacent cores within the molecular system are already included in the calculation, only contributions from charged atoms outside the molecular system are included in the potential, $V_\mathrm{A}^l$. The Ewald method [9], following the derivation by Slater and De Cicco [10], is used to evaluate the lattice potentials.

The formalism for the calculation of exciton splittings in crystals has been given many times before [11]. A brief re-capitulation of some of the formulae used is given below. In all calculations $V_{le}$ is included in the single molecule Hamiltonian. The excited state crystal wave functions [11] for $k=0$ are given in

Table 1. *Wave-Functions for crystals of* $D_{2h}^{16}$ *symmetry* ($k=0$)

| Site group symmetry | Factor group symmetry | Linear combinations of one site excitons | Site group symmetry | Factor group symmetry | Linear combinations of one site excitons |
|---|---|---|---|---|---|
| $A'$ | $A_{1g}$ | $\phi_1^f+\phi_2^f+\phi_3^f+\phi_4^f$ | $A''$ | $A_{1u}$ | $\phi_1^f+\phi_2^f+\phi_3^f+\phi_4^f$ |
| | $B_{2g}$ | $\phi_1^f+\phi_2^f-\phi_3^f-\phi_4^f$ | | $B_{2u}$ | $\phi_1^f+\phi_2^f-\phi_3^f-\phi_4^f$ |
| | $B_{1u}$ | $\phi_1^f-\phi_2^f+\phi_3^f-\phi_4^f$ | | $B_{1g}$ | $\phi_1^f-\phi_2^f+\phi_3^f-\phi_4^f$ |
| | $B_{3u}$ | $\phi_1^f-\phi_2^f-\phi_3^f+\phi_4^f$ | | $B_{3g}$ | $\phi_1^f-\phi_2^f-\phi_3^f+\phi_4^f$ |

Table 1 where $\phi_\alpha^f$ is a one site exciton wave function for the $f^{\text{th}}$ excited state at the $\alpha^{\text{th}}$ site. The plane of symmetry for the site group ($C_s$) is the $xz$ plane. The molecular axes system is the same as used previously [2] except that the axes on the central atom have been rotated by 45° about the $z$ axis. Thus as can be seen from Table 1, each site molecule ${}^1A' \leftarrow {}^1A'$ transition gives rise to two allowed transitions ($B_{1u}$ and $B_{3u}$) and each ${}^1A'' \leftarrow {}^1A'$ transition gives rise to one allowed transition ($B_{2u}$). Since the molecular axes are parallel to the crystal axes, these transitions will be polarized as $B_{1u}$ ($z$ crystal axis), $B_{2u}$ ($y$ crystal axis) and $B_{3u}$ ($x$ crystal axis).

The expressions for the diagonal elements of the excited state Hamiltonian matrix are [12]

$$H_\alpha^f = \varepsilon_0^f + D_\alpha^f + M_\alpha^f \tag{5}$$

where $\varepsilon_0^f$ is the excitation energy (corresponding to the $f^{\text{th}}$ excited state) for a transition localized on a single isolated molecule, $D_\alpha^f$ is the difference between the electrostatic energies of the ground state and the $f^{\text{th}}$ excited state at the $\alpha^{\text{th}}$ site and $M_\alpha^f$ is a term which includes the exciton splitting [13]. Specifically $D_\alpha^f$ and $M_\alpha^f$ are given by

$$D_\alpha^f = \sum_{\substack{m \\ m\neq n \text{ when} \\ \beta=\alpha}} \sum_{\beta} (\langle \phi_{n\alpha}^f \phi_{m\beta}^0 | V_{n\alpha,m\beta} | \phi_{n\alpha}^f \phi_{m\beta}^0 \rangle - \langle \phi_{n\alpha}^0 \phi_{m\beta}^0 | V_{n\alpha,m\beta} | \phi_{n\alpha}^0 \phi_{m\beta}^0 \rangle \tag{6}$$

and

$$M_\alpha^f = \sum_{\substack{m \\ m\neq n \text{ when} \\ \alpha=\beta}} \sum_{\beta} B_\alpha^{g*} B_\beta^g \langle \phi_{n\alpha}^f \phi_{m\beta}^0 | V_{n\alpha,m\beta} | \phi_{n\alpha}^0 \phi_{m\beta}^f \rangle \tag{7}$$

where

$\phi_{n\alpha}^f$ is the molecular wave function for a molecule at the $\alpha^{\text{th}}$ site in the $n^{\text{th}}$ unit cell in the $f^{\text{th}}$ excited state ($\phi_{n\alpha}^0$ is the ground state for the same molecule),

$V_{n\alpha,m\beta}$ is the interaction potential between molecules at the $\alpha^{\text{th}}$ site in the $n^{\text{th}}$ unit cell and the $\beta^{\text{th}}$ site in the $m^{\text{th}}$ unit cell,

$B_\alpha^g$ is the coefficient with which the one site exciton wave-functions for the $\alpha^{\text{th}}$ site occurs in the $g^{\text{th}}$ factor group crystal wavefunction corresponding to the $f^{\text{th}}$ excited molecular state.

Because of the complexity of excited state wave-functions of a transition metal oxyanion it is not feasible to evaluate the integrals in (6) and (7) directly. Instead we have evaluated them using the multipole expansion technique[1], a method which has the advantage that the form of the wave-functions need not be known. We have made the usual approximation of taking just the dipole-dipole term in the expansion.

Unfortunately the $D_\alpha^f$ integrals cannot be evaluated by this method. It is reasonable to assume that the $D_\alpha^f$ values for crystal transitions arising from the same transition of the isolated molecule are the same. If crystal field mixing with transitions arising from other isolated molecule transitions is small, as is often the case, then this term is simply a band-shift term and effectively cancels in exciton splitting calculations, thus not affecting interpretations of spectra.

The dipole-dipole sums involved in the calculation of exciton splitting are calculated in the following way: the interaction between two ideal point dipoles $n$ and $n'$ with components $n_x$, $n_y$, $n_z$ and $n'_x$, $n'_y$, $n'_z$ may be written as [15]

$$I_{nn'} = -F_x^n n'_x - F_y^n n'_y - F_z^n n'_z \tag{8}$$

where $F_x^n$, $F_y^n$, and $F_z^n$ are the components of the electric field in the $x$, $y$, and $z$ directions at the origin of $n'$ due to dipole $n$ and

$$F_x^n = \left(\frac{3x^2 - R^2}{R^5}\right) n_x + \frac{3xy}{R^5} n_y + \frac{3xz}{R^5} n_z \,, \tag{9}$$

$$F_y^n = \frac{3xy}{R^5} n_x + \left(\frac{3y^2 - R^2}{R^5}\right) n_y + \frac{3yz}{R^5} n_z \,, \tag{10}$$

$$F_z^n = \frac{3xy}{R^5} n_x + \frac{3yz}{R^5} n_y + \left(\frac{3z^2 - R^2}{R^5}\right) n_z \tag{11}$$

where $R^2 = x^2 + y^2 + z^2$.

Written in this form the components of the electric field at a point due to a "sea" of dipoles converge rapidly when summed over a sphere [16]. The dipole-dipole interaction term for the crystal then becomes

$$I = -n'_x \sum_n F_x^n - n'_y \sum_n F_y^n - n'_z \sum_n F_z^n \ldots . \tag{12}$$

The dipole-dipole sums for potassium permanganate for a transition dipole length of 1 Å are given in Table 2[2].

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[1] This technique involves the assumption that the potential is the interaction between two non-overlapping charge distributions. For many crystals the charge distributions cannot be considered as non-overlapping. If the overlap is large then the integrals must be evaluated directly but if the overlap is small the usual practice has been to neglect it. For ionic crystals the neglect of all overlap is quite a drastic approximation because of the large charge separations that occur in ionic molecules. We are investigating the use of the more complex slightly overlapping charge clouds expansion [14] for use with ionic crystals.

[2] Difficulties have been reported in the literature in getting dipole-dipole sums to converge. As a check that Eq. (12) when summed over a sphere does converge properly the dipole-dipole sums for benzene were evaluated. These were compared with the values published by Thirunamachandran [17] which were evaluated for an infinite crystal using the complex Ewald-Kornfeld method [18]. The sums converged to within 1% of the Thirunamachandran values inside 30 Å.

Table 2. *Dipole-Dipole sums for potassium permanganate* ($cm^{-1}$ $Å^{-2}$)

| | *aa* | *bb* | *cc* | *ab*[a] | *ac* | *bc* |
|---|---|---|---|---|---|---|
| 1.1[b] | 1373 | −1698 | 324 | 0 | 0 | 0 |
| 1.2 | 3376 | 1076 | 2300 | 0 | −1034 | 0 |
| 1.3 | 638 | − 818 | − 180 | 0 | 0 | 0 |
| 1.4 | −4220 | −1942 | −2279 | 0 | 0 | 0 |

[a] Interaction between two dipoles, one pointing along the *a* crystal axis and the other along the *b* crystal axis.

[b] Entries in row (1.1) correspond to sums over translationally equivalent molecules, for the other rows between translationally inequivalent molecules.

## Results and Discussion

The redistribution of electron densities that occur when the effects of crystal lattices are added to calculations for the isolated permanganate and chromate ions are given in Table 3. The CNDO 1 parameter scheme [2] was used for the permanganate calculations, and the CNDO 10 parameter scheme [2] for the chromate calculations. The numbers in Table 3 are given to more significant figures than is probably warranted for these calculations, so that the trends can be seen better (compare corresponding tables in Ref. [2] and [3]). For permanganate there is no significant change in the central atom charge in going from the isolated ion to the crystal, while there are changes in the charges on the oxygen atoms, this reflecting their crystallographic inequivalence in the crystal. The latter also occurs for chromate and, in addition, there is a noticeable increase of charge on the central atom going from the isolated anion to the crystals. From Table 4 it can be seen that there are only small changes in the central atom-oxygen bond energies. The effects of the potassium permanganate lattice on the molecular orbitals and lowest energy singlet spectroscopic states are shown in Tables 5 and 6 respectively. The molecular orbital splittings are small, usually less than 0.1 eV,

Table 3. *Crystal lattice effects on electron densities in the permanganate and chromate ions*

| Atomic charges | Isolated $MnO_4^-$ | $KMnO_4$ | Isolated $CrO_4^{2-}$ | $K_2CrO_4$ | $CsCrO_4$ |
|---|---|---|---|---|---|
| Central atom | +0.167 | 0.171 | −0.182 | −0.867 | −0.852 |
| $O_1$ | −0.292 | −0.278 | −0.297 | −0.211 | −0.247 |
| $O_2$ | −0.292 | −0.261 | −0.297 | −0.314 | −0.299 |
| $O_3$ | −0.292 | −0.316 | −0.297 | −0.304 | −0.300 |
| $O_4$ | −0.292 | −0.316 | −0.297 | −0.304 | −0.300 |
| Central atomic orbital occupations 4*s* | 0.098 | 0.098 | 0.095 | 0.097 | 0.096 |
| Each 4*p* | 0.005 | 0.005 | 0.052 | 0.054 | 0.053 |
| Total 4*p* | 0.015 | 0.015 | 0.156 | 0.162 | 0.159 |
| Each $3d_\sigma$ | 1.528 | 1.527 | 1.469 | 1.476 | 1.475 |
| Each $3d_\pi$ | 1.068 | 1.067 | 1.077 | 1.090 | 1.086 |
| Total 3*d* | 6.720 | 6.715 | 6.561 | 6.608 | 6.597 |

Table 4. *Crystal lattice effects on bond and total energies in the permanganate and chromate ions*

| Energy | Isolated $MnO_4^-$ | $KMnO_4$ | Isolated $CrO_4^{2-}$ | $K_2CrO_4$ | $Cs_2CrO_4$ |
|---|---|---|---|---|---|
| Total | −2397 | −2536 | −2155 | −2435 | −2453 |
| Bond $E_{CA,O_1}$ [a] | − 224.62 | − 224.48 | − 190.04 | − 189.73 | − 189.45 |
| Bond $E_{CA,O_2}$ | − 224.62 | − 224.46 | − 190.04 | − 190.18 | − 190.36 |
| Bond $E_{CA,O_3}$ | − 224.62 | − 224.75 | − 190.04 | − 190.19 | − 190.26 |
| Bond $E_{CA,O_4}$ | − 224.62 | − 224.75 | − 190.04 | − 190.19 | − 190.26 |

[a] CA−central atom.

Table 5. *Crystal lattice effects on the molecular orbitals of the permanganate ion in the potassium permanganate lattice*

| $T_d$ (Isolated) | | $C_s$ (Crystal) | |
|---|---|---|---|
| MO Symmetry | Eigenvalue eV | MO Symmetry | Eigenvalue eV |
| $t_2$ | 62.501 | $a'$ | 56.732 |
| | | $a''$ | 56.727 |
| | | $a'$ | 56.725 |
| $a_1$ | 42.264 | $a'$ | 36.502 |
| $t_2$ | 11.745 | $a'$ | 6.038 |
| | | $a'$ | 5.944 |
| | | $a''$ | 9.914 |
| $e$ | 5.577 | $a''$ | − 0.196 |
| | | $a'$ | − 0.198 |
| $t_1$ | − 3.726 | $a'$ | − 9.433 |
| | | $a''$ | − 9.476 |
| | | $a''$ | − 9.617 |
| $a_1$ | − 4.421 | $a'$ | −10.202 |
| $t_2$ | − 5.340 | $a'$ | −11.089 |
| | | $a''$ | −11.138 |
| | | $a'$ | −11.147 |
| $e$ | −10.649 | $a'$ | −16.422 |
| | | $a''$ | −16.427 |
| $t_2$ | −11.195 | $a'$ | −16.965 |
| | | $a''$ | −16.969 |
| | | $a'$ | −16.975 |

and overall, the energy levels have been lowered about 5 eV. The spectroscopic state splittings are somewhat larger, up to 0.5 eV and overall there is a shift to higher energies of less than 1 eV.

Similar results were obtained for the chromate ion in the potassium chromate and cesium chromate lattices. In Fig. 1, the predicted splittings of the isolated permanganate and chromate ion spectra are shown. It should be noted that this splitting is of the electronic states and not of each individual vibronic band (both the permanganate and chromate spectra show considerable vibrational structure [19–22]).

Table 6. *Crystal lattice effects on the lowest energy singlet transitions of the permanganate ion in the potassium permanganate lattice*

| $T_d$ (Isolated) | | $C_s$ (Crystal) | |
|---|---|---|---|
| Transition | Energy eV | Transition | Energy eV |
| $T_1 \leftarrow A_1$ | 1.476 | $A'' \leftarrow A'$ | 1.590 |
| | | $A' \leftarrow A'$ | 1.693 |
| | | $A'' \leftarrow A'$ | 1.697 |
| $E \leftarrow A_1$ | 2.020 | $A' \leftarrow A'$ | 1.992 |
| | | $A'' \leftarrow A'$ | 2.028 |
| $T_2 \leftarrow A_1$ | 2.161 | $A' \leftarrow A'$ | 2.135 |
| | | $A'' \leftarrow A'$ | 2.145 |
| | | $A' \leftarrow A'$ | 2.151 |
| $T_1 \leftarrow A_1$ | 2.991 | $A'' \leftarrow A'$ | 3.169 |
| | | $A' \leftarrow A'$ | 3.180 |
| | | $A'' \leftarrow A'$ | 3.220 |
| $T_2 \leftarrow A_1$ | 4.132 | $A' \leftarrow A'$ | 3.767 |
| | | $A'' \leftarrow A'$ | 4.128 |
| | | $A' \leftarrow A'$ | 4.152 |
| $E \leftarrow A_1$ | 5.093 | $A' \leftarrow A'$ | 5.077 |
| | | $A'' \leftarrow A'$ | 5.132 |
| $T_2 \leftarrow A_1$ | 5.831 | $A' \leftarrow A'$ | 5.949 |
| | | $A'' \leftarrow A'$ | 6.151 |
| | | $A' \leftarrow A'$ | 6.657 |
| $T_1 \leftarrow A_1$ | 6.843 | $A' \leftarrow A'$ | 7.121 |
| | | $A'' \leftarrow A'$ | 7.145 |
| | | $A'' \leftarrow A'$ | 7.162 |

For a molecule in a mixed crystal system, where the lowest energy host exciton band is considerably higher in energy than the transitions being investigated, the effects of the crystal lattice on these transitions is limited to site group splittings. Suitable mixed crystal systems for the molecules in question are $KMnO_4/KClO_4$ and $K_2CrO_4/K_2SO_4$. Extensive experimental data on the $KMnO_4/KClO_4$ has been accumulated [21, 22], especially for the first band system at 2.27 eV.

The potassium perchlorate [23] and potassium permanganate crystal structures are almost identical. They belong to the same space group, have the same number of molecules per unit cell, and have unit cell dimensions within 5%. The potential at any point in the potassium perchlorate lattice for a unit positive charge at each lattice site is within 1% of that at the equivalent point in the potassium permanganate lattice. If the assumption is made that the charges on the atoms in the potassium perchlorate lattice are the same as those found on the equivalent atoms in the potassium permanganate lattice then the predicted mixed crystal site group splittings will be as given in Table 7 for the pure potassium permanganate crystal.

Table 7 shows a comparison of these values for the first band system with those experimentally observed. The agreement is qualitative only. Possible reasons for the quantitative disagreement are: Firstly, the true O–O bands may not have been experimentally observed. This could be checked by a comparison of the

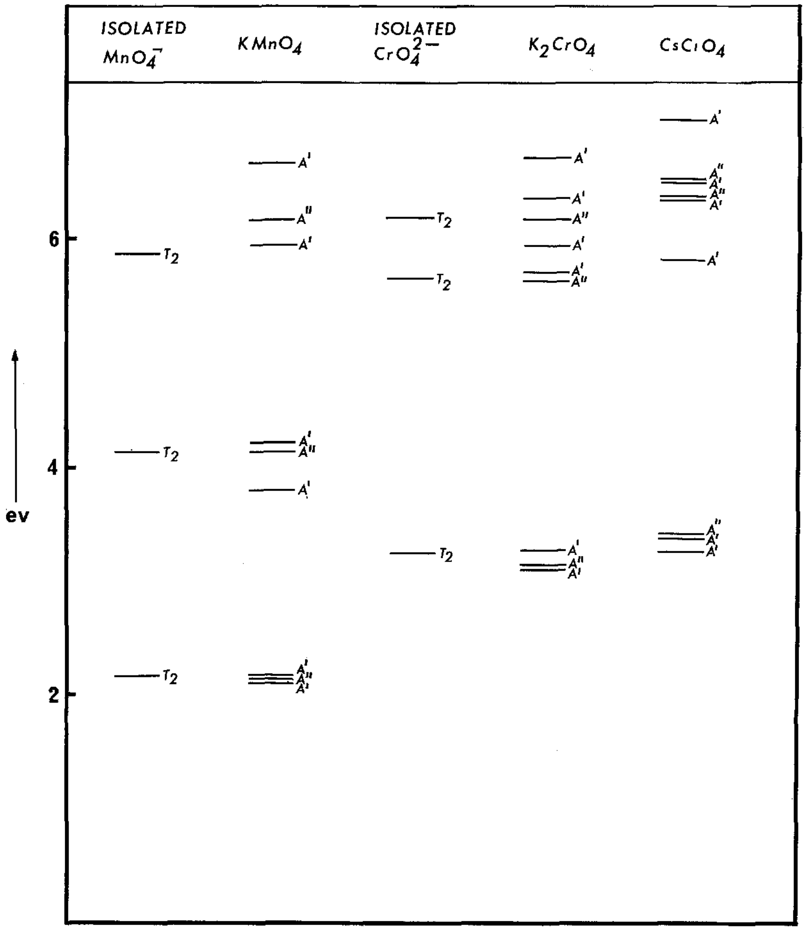

Fig. 1. Allowed levels for isolated ions and predicted splittings for these ions in crystal lattices

fluorescence and absorption spectra (however we have been unable to detect fluorescence at 77° K). Secondly, the assumption that the charges on the equivalent atoms in the potassium permanganate and potassium perchlorate lattices are the same may be grossly incorrect. This is further complicated by the suspicion that CNDO calculations involving *d*-orbitals do not give good values of atomic charges [2]. Thirdly, the point charge approximation used in the Ewald method for evaluating lattice potentials is a poor one. The major contributions to the potential at a point is due to the atoms nearest that point – the very atoms for which the point charge approximation is the poorest.

The predicted exciton splitting of the $^1A' \leftarrow {}^1A'$ transition of the permanganate ion in the potassium permanganate lattice arising from the lowest energy symmetry-allowed $^1T_2 \leftarrow {}^1A_1$ transition of the isolated ion is given in Table 8. Mixing in of transitions arising from higher energy $^1T_2 \leftarrow {}^1A_1$ transitions of the isolated molecule has been omitted. As $^1A' \leftarrow {}^1A'$ transitions under $C_s$ symmetry are

Table 7. *Calculated and experimental energies of the site group transitions of the permanganate ion in the* $KMnO_4/KClO_4$ *mixed crystal system arising from the lowest energy symmetry-allowed* ${}^1T_2 \leftarrow {}^1A_1$ *transition of the isolated molecule*

| Transition | Polarization | Energy eV | |
|---|---|---|---|
| | | Calculated | Experimental [21] |
| ${}^1A' \leftarrow {}^1A'$ | *ab* plane[a] | 2.1354 | 2.2405 |
| ${}^1A'' \leftarrow {}^1A'$ | *c* axis | 2.1452 | 2.2402 |
| ${}^1A' \leftarrow {}^1A'$ | *ab* plane[a] | 2.1514 | 2.2430 |

[a] Has been measured experimentally along the *a* axis only [21].

Table 8. *Exciton splitting of the* ${}^1A' \leftarrow {}^1A'$ *transitions of the permanganate ion in the potassium permanganate lattice originating from the lowest energy* ${}^1T_2 \leftarrow {}^1A_1$ *transition of the isolated ion*

| Transition | Transition Energy eV | Exciton splitting eV | |
|---|---|---|---|
| | | *a* Axis polarized | *b* Axis polarized |
| ${}^1A' \leftarrow {}^1A'$ | $2.1354 + D_f$ | 0.0636 | 0.0195 |
| ${}^1A' \leftarrow {}^1A'$ | $2.1514 + D_f$ | 0.0284 | 0.0017 |

polarized in the *ab* crystal plane the exciton splitting will be somewhere between the two limiting values given in Table 8.

The first band system of the permanganate ion has extensive vibrational fine structure – some 60 or so vibronic bonds have been resolved for the permanganate ion in the $KMnO_4/KClO_4$ mixed crystal lattice [21]. When the coupling between molecules is weak, as it is between permanganate ions, the exciton splitting of a vibronic level to a first approximation is proportional to the intensity of that vibronic transition rather than to the intensity of the complete band system. Accordingly, the exciton splitting of the individual vibronic bonds will be between 1/10th and 1/100th of the values given in Table 8.

Only one systematic study of the permanganate spectrum in pure crystals has been carried out. This was made by Teltow in 1938 [22]. He measured the spectrum at temperatures down to 20° K but did not identify any exciton splitting.

## Conclusions

The method used in this paper to calculate the effect of the electrostatic environment on the excited states of molecular ions in crystals needs further development. However the present treatment shows the sort of splitting one should expect. Calculations to show these splittings have been made for the crystals for which the atomic positions are accurately known. However these are not the crystals for which absorption spectra are available. Hence a really meaningful comparison is not possible. We have however compared the spectrum of $KMnO_4/KClO_4$ with the calculations for $KMnO_4$ crystal. A calculation of factor-group splitting of excited states using the dipole-dipole approximation in a tight-binding exciton model predicts observable splittings. These have not been experimentally observed.

One feature of the present calculations is that the electrostatic field of the lattice stabilizes the molecular orbitals of the anions by more than 5 eV. In the absence of the lattice the uppermost filled molecular orbital for the ground state of the anion is scarcely bonding. This seems to be a physically realistic result for an isolated anion but all previous calculations on these isolated anions (see convenient summary in Fig. 10 of [24]) have implied that the uppermost filled orbital was very strongly bonding, perhaps because previous calculations have not adequately allowed for interelectronic repulsion.

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